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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
62/266,411	12/11/2015		260	SP15-410PZ		

CONFIRMATION NO. 7699

FILING RECEIPT

OC000000080344163

22928
CORNING INCORPORATED
SP-TI-3-1
CORNING, NY 14831

Date Mailed: 02/05/2016

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The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 62/266,411**

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No
Title

FUSION-FORMABLE, GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53(c).

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TITLE OF THE INVENTION (280 characters max)

FUSION-FORMABLE GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT

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ENCLOSED APPLICATION PARTS (*check all that apply*)

☒ Specification *Number of Pages:* 68	☐ Small Entity Statement
☒ Drawing(s) *Number of Pages:* 22	☐ Other (specify):

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (*check one*)

☐ A check or money order is enclosed to cover the filing fees. ☒ Corning Incorporated hereby authorizes charges for filing fees and any additional fees required or credit overpayment to Deposit Account Number: 03-3325	FILING FEE AMOUNT $260.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

____.

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PROVISIONAL APPLICATION COVER SHEET

Additional Page

Respectfully submitted,

SIGNATURE: Payal Patel Date: 12/11/2015
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on 12/11/15

Signature Shana Wilson

Shana Wilson

FUSION-FORMABLE, GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT

BACKGROUND

[0001] This disclosure relates to fusion-formable, glass-based articles exhibiting improved damage resistance, including improved fracture resistance, and more particularly to fusion-formable, glass and glass ceramic articles exhibiting a non-zero metal oxide concentration gradient or concentration that varies along a substantial portion of the thickness.

[0002] Glass-based articles often experience severe impacts that can introduce large flaws into a surface of such articles. Such flaws can extend to depths of up to about 200 micrometers from the surface. Traditionally, thermally tempered glass has been used to prevent failures caused by the introduction of such flaws into the glass because thermally tempered glass often exhibits large compressive stress (CS) layers (e.g., approximately 21% of the total thickness of the glass), which can prevent the flaws from propagating further into the glass and thus, can prevent failure. An example of a stress profile generated by thermal tempering is shown in Figure 1. In Figure 1, the thermally treated glass article 100 includes a first surface 101, a thickness t_1, and a surface CS 110. The thermally treated glass article 100 exhibits a CS that decreases from the first surface 101 to a depth of layer (DOL) 130, as defined herein, at which depth the stress changes from compressive to tensile stress and reaches a maximum central tension (CT) 120.

[0003] Thermal tempering is currently limited to thick glass-based articles (i.e., glass-based articles having a thickness t_1 of about 3 millimeters or greater) because, to achieve the thermal strengthening and the desired residual stresses, a sufficient thermal gradient must be formed between the core of such articles and the surface. Such thick articles are undesirable or not practical in many applications such as display (e.g., consumer electronics, including mobile phones, tablets, computers, navigation systems, and the like), architecture (e.g., windows, shower panels, countertops etc.), transportation (e.g., automotive, trains, aircraft, sea craft, etc.), appliance, or any application that requires superior fracture resistance but thin and light-weight articles.

[0004] Although chemical strengthening is not limited by the thickness of the glass-based article in the same manner as thermally tempering, known chemically strengthened glass-based articles do not exhibit the stress profile of thermally tempered glass-based articles. An example of a stress profile generated by chemical strengthening (e.g., by an ion exchange

process), is shown in Figure 2. In Figure 2, the chemically strengthened glass-based article 200 includes a first surface 201, a thickness t_2 and a surface CS 210. The glass-based article 200 exhibits a CS that decreases from the first surface 201 to a DOC 230, as defined herein, at which depth the stress changes from compressive to tensile stress and reaches a maximum CT 220. As shown in Figure 2, such profiles exhibit a substantially flat CT region or CT region with a constant or near constant tensile stress along at least a portion of the CT region. Often, known chemically strengthened glass-based articles exhibit a lower maximum CT value, as compared to the maximum central value shown in Figure 1.

[0005] Accordingly, there is a need for thin glass-based articles that exhibit improved fracture resistance.

SUMMARY

[0006] A first aspect of this disclosure pertains to a glass-based article including a first surface and a second surface opposing the first surface defining a thickness (t), a concentration of a metal oxide that is both non-zero and varies along a thickness range from about $0 \cdot t$ to about $0.3 \cdot t$; and a central tension (CT) region comprising a maximum CT of less than about 80 MPa. In one or more embodiments, the when the glass-based article is fractured, the glass-based article fractures into at least 2 fragments/inch^2. In one or more embodiments, when the glass-based article is fractured, the glass-based article fractures into at least 1 fragment/inch^2 up to 40 fragments/inch^2.

[0007] In one or more embodiments, the concentration of the metal oxide is non-zero and varies along the entire thickness. In one or more embodiments, the metal oxide generates a stress along the thickness range. The metal oxide may have the largest ionic diameter of all of the total metal oxides in the glass-based substrate. The concentration of the metal oxide may decrease from the first surface to a point between the first surface and the second surface and increases from the point to the second surface. For example, the concentration of the metal oxide at the first surface may be about 1.5 times greater than the concentration of the metal oxides at a depth equal to about $0.5 \cdot t$. In some instances, the concentration of the metal oxide is about 0.05 mol% or greater throughout the thickness (e.g., in the range from about 1 mol% to about 15 mol%). The metal oxide may include any one or more of Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O. In one or more embodiments, the metal oxide concentration gradient may be present in the CT region of the glass-based article.

[0008] In one or more embodiments, the glass-based article includes a stress profile extending along the thickness, wherein all points of the stress profile between a thickness

range from about 0•*t* up to 0.3•*t* and from greater than 0.7•*t*, comprise a tangent that is less than about -0.1 MPa/micrometers or greater than about 0.1 MPa/micrometers. In some embodiments, the stress profile comprises a maximum CS, a DOC and a maximum CT of less than about 80 MPa, wherein the ratio of maximum CT to maximum CS is in the range from about 0.01 to about 0.2 and wherein the DOC is about 0.1•*t* or greater. When the glass-based article of one or more embodiments is fractured, the glass-based article fractures into at least 2 fragments/inch^2.

[0009] The glass-based article of one or more embodiments may include a surface compressive stress (CS) of about 300 MPa or greater or about 500 MPa or greater. In some embodiments, the glass-based article includes a surface CS of about 200 MPa or greater and a chemical depth of layer of about 0.4•*t* or greater. In one or more embodiments, the CS may extend from the first surface to a DOC, wherein the DOC is about 0.1•*t* or greater. The glass-based article of some embodiments exhibits a ratio of maximum CT to surface CS (which may include the maximum CS) in the range from about 0.01 to about 0.2. Optionally, the surface CS is greater than the maximum CT.

[0010] In one or more embodiments, the glass-based article includes a first metal oxide concentration and a second metal oxide concentration, wherein the first metal oxide concentration is in the range from about 0 mol% to about 15 mol% from a first thickness range from about 0•*t* to about 0.5•*t*, and wherein the second metal oxide concentration is in the range from about 0 mol% to about 10 mol% from a second thickness range from about 0 micrometers to about25 micrometers. Optionally, the glass-based article includes a third metal oxide.

[0011] In one or more embodiments, the glass-based article includes a concentration of a metal oxide that is both non-zero and varies along a thickness range from about 0•*t* to about 0.3•*t* (or from about 0•*t* to about 0.4•*t* or from about 0•*t* to about 0.45•*t*), a surface compressive stress of greater than about 200MPa or greater; and a CT region having a maximum CT of less than about 80 MPa.

[0012] The glass-based article may have a thickness *t* of about 3 millimeters or less or about 1 millimeter or less. The glass-based article may have an amorphous structure, a crystalline structure or a combination of both. The glass-based article may exhibit a transmittance of about 88% or greater over a wavelength in the range from about 380 nm to about 780 nm. Moreover, in some embodiments, the glass-based article may exhibit a CIELAB color space coordinates, under a CIE illuminant F02, of L* values of about 88 and

greater, a* values in the range from about -3 to about +3, and b* values in the range from about -6 to about +6.

[0013] In one or more embodiments, the glass-based article includes a Young's modulus of less than 80 GPa. The glass-based article includes a liquidus viscosity of about 100 kilopoise (kP) or greater.

[0014] The glass-based article may include a composition having any one or more of: a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%, a composition comprising greater than about 4 mol% Na_2O, a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and a composition comprising a non-zero amount of P_2O_5.

[0015] The glass-based article may include a diffusivity of about 450 μm^2/hour or greater at about 460 °C and a DOC greater than about 0.15•*t*, and wherein the surface CS is 1.5 times the maximum CT or greater.

[0016] In some embodiments, the glass-based article comprises a fracture toughness (K_{1C}) of about 0.7 MPa·$m^{1/2}$ or greater.

[0017] In one or more embodiments, the glass-based article exhibits a stored tensile energy of about greater than 0 J/m2 to less than 20 J/m^2.

[0018] In one or more embodiments, the glass-based article includes a stress profile including a CS region and a CT region, wherein the CT region is defined by the equation Stress(x) = MaxCT – (((MaxCT • (n+1))/0.5^n)•|$(x/t)-0.5|^n$), wherein MaxCT is a maximum CT value and provided as a positive value in units of MPa, x is position along the thickness (*t*) in micrometers, and n is between 1.5 and 5. In some embodiments, the CT region comprises a maximum CT value in the range from about 50 MPa to about 250 MPa and the maximum CT value is at a depth in the range from about 0.4*t* to about 0.6*t*. In some instances, from a thickness in the range from about 0*t* to about 0.1*t* microns, the stress profile comprises a slope in the range from about 20 MPa/microns to about 200 MPa/microns. In one or more embodiments, the stress profile is defined by a plurality of error functions as measured from 0.5t to the surface.

[0019] A second aspect of this disclosure pertains to the use of a glass composition in a strengthened glass-based article, comprising (in mol%): SiO_2 in an amount in the range from about 60 to about 75, Al_2O_3 in an amount in the range from about 12 to about 20, B_2O_3 in an amount in the range from about 0 to about 5, Li_2O in an amount in the range from about 2 to about 8, Na_2O in an amount greater than 4, P_2O_5 in a non-zero amount, MgO in an amount in

the range from about 0 to about 5, ZnO in an amount in the range from about 0 to about 3, CaO in an amount in the range from about 0 to about 5, wherein the glass composition is ion-exchangeable and is amorphous, wherein the total amount of Al_2O_3 and Na_2O is greater than about 15 mol%, wherein the glass composition is substantially free of nucleating agents, and wherein the glass composition comprises a liquidus viscosity of about 100 kP or greater. In one or more embodiments, the glass composition is substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO.

[0020] A third aspect of this disclosure pertains to a glass substrate comprising a composition including, in mol%, SiO_2 in an amount in the range from about 60 to about 75, Al_2O_3 in an amount in the range from about 12 to about 20, B_2O_3 in an amount in the range from about 0 to about 5, Li_2O in an amount in the range from about 2 to about 8, Na_2O in an amount greater than about 4, MgO in an amount in the range from about 0 to about 5, ZnO in an amount in the range from about 0 to about 3, CaO in an amount in the range from about 0 to about 5, and P_2O_5 in a non-zero amount; wherein the glass substrate is ion-exchangeable and is amorphous, wherein total amount of Al_2O_3 and Na_2O in the composition is greater than about 15 mol%, wherein the glass composition is substantially free of nucleating agents and comprises a liquidus viscosity of about 100 kP or greater.

[0021] In some embodiments, the glass substrate is amorphous and is strengthened, wherein the Na_2O concentration varies, wherein the composition is substantially free of nucleating agents, total amount of Al_2O_3 and Na_2O in the composition is greater than about 15 mol%, wherein the glass composition is substantially free of nucleating agents, and comprises a liquidus viscosity of about 100 kP or greater. In some embodiments the glass substrate includes a non-zero amount of P_2O_5.

[0022] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0023] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary, and are intended to provide an overview or framework to understanding the nature and character of the claims. The accompanying drawings are included to provide a further understanding, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s), and together with the description serve to explain principles and operation of the various embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Figure 1 is a cross-sectional view across a thickness of a known, thermally tempered glass article;

[0025] Figure 2 is a cross-sectional view across a thickness of a known, chemically strengthened glass article;

[0026] Figure 3 is a cross-sectional view across a thickness of a chemically strengthened glass-based article according to one or more embodiments of this disclosure;

[0027] Figure 4 is a is a schematic cross-sectional view of a ring-on-ring apparatus;

[0028] Figure 5 is a graph showing the maximum CT values for Examples 1A-1G as a function of ion exchange time;

[0029] Figure 6 is a graph showing the measured stress of Example 1E as a function of depth extending from the surface of the glass-based article of Example 1E into the glass-based article;

[0030] Figure 7 is a graph showing the load to failure values for glass-based articles according to Example 2A after being abraded at different loads or pressures;

[0031] Figure 8 is a graph showing the heights at which the glass-based articles according to Example 2A failed after being dropped onto 180 grit sandpaper and then onto 30 grit sandpaper;

[0032] Figure 9 is a graph showing the heights at which the glass-based articles according to Example 3A and Comparative Example 3B failed after being dropped onto 30 grit sandpaper;

[0033] Figure 10 is a graph comparing the average load to failure of glass-based articles according to Example 3A and Comparative Example 3B, after being abraded at a load or pressure of 25 psi;

[0034] Figure 11 is a graph comparing the average load to failure of glass-based articles according to Example 3A and Comparative Example 3B, after being abraded at a load or pressure of 45 psi;

[0035] Figure 12 is a graph showing the stress profiles of Examples 4A-1 through 4A-6 as a function of depth;

[0036] Figure 13 is a graph showing the maximum CT and DOC values of Examples 4A-1 through 4A-6 as a function of ion exchange time;

[0037] Figure 14 is a graph showing the stress profiles of Examples 4B-1 through 4B-6 as a function of depth;

[0038] Figure 15 is a graph showing the maximum CT and DOC values of Examples 4B-1 through 4B-6 as a function of ion exchange time;

[0039] Figure 16 is a graph showing the stress profiles of Examples 4C-1 through 4C-6 as a function of depth;

[0040] Figure 17 is a graph showing the maximum CT and DOC values of Examples 4C-1 through 4C-6 as a function of ion exchange time;

[0041] Figure 18 is a graph showing the stress profiles of Examples 4D-1 through 4D-6 as a function of depth;

[0042] Figure 19 is a graph showing the maximum CT and DOC values of Examples 4D-1 through 4D-6 as a function of ion exchange time;

[0043] Figure 20 is a graph showing the stress profiles of Comparative Example 5A and Example 5B as a function of depth;

[0044] Figure 21 is a graph showing the stored tensile energy of Comparative Example 5A and Example 5B as a function of maximum CT; and

[0045] Figure 22 is a graph showing stored tensile energy of Comparative Example 5C and Example 5D as a function of maximum CT.

DETAILED DESCRIPTION

[0046] Reference will now be made in detail to various embodiments, examples of which are illustrated in the accompanying examples and drawings.

[0047] In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also understood that, unless otherwise specified, terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms. In addition, whenever a group is described as comprising at least one of a group of elements and combinations thereof, it is understood that the group may comprise, consist essentially of, or consist of any number of those elements recited, either individually or in combination with each other. Similarly, whenever a group is described as consisting of at least one of a group of elements or combinations thereof, it is understood that the group may consist of any number of those elements recited, either individually or in combination with each other. Unless otherwise specified, a range of values, when recited, includes both the upper and

lower limits of the range as well as any ranges therebetween. As used herein, the indefinite articles “a,” “an,” and the corresponding definite article “the” mean “at least one” or “one or more,” unless otherwise specified. It also is understood that the various features disclosed in the specification and the drawings can be used in any and all combinations.

[0048] As used herein, the terms “glass-based article” and “glass-based substrates” are used in their broadest sense to include any object made wholly or partly of glass. Glass-based articles include laminates of glass and non-glass materials, laminates of glass and crystalline materials, and glass-ceramics (including an amorphous phase and a crystalline phase). Unless otherwise specified, all compositions are expressed in terms of mole percent (mol%).

[0049] It is noted that the terms "substantially" and "about" may be utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation. These terms are also utilized herein to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue. Thus, for example, a glass-based article that is “substantially free of MgO” is one in which MgO is not actively added or batched into the glass-based article, but may be present in very small amounts as a contaminant.

[0050] Unless otherwise specified, all temperatures are expressed in terms of degrees Celsius (°C). As used herein the term “softening point” refers to the temperature at which the viscosity of a glass is approximately $10^{7.6}$ poise (P), the term “anneal point” refers to the temperature at which the viscosity of a glass is approximately $10^{13.2}$ poise, the term “200 poise temperature (T^{200P})” refers to the temperature at which the viscosity of a glass is approximately 200 poise, the term “10^{11} poise temperature ” refers to the temperature at which the viscosity of a glass is approximately 10^{11} poise, the term “35 kP temperature (T^{35kP})” refers to the temperature at which the viscosity of a glass is approximately 35 kilopoise (kP), and the term “160 kP temperature (T^{160kP})” refers to the temperature at which the viscosity of a glass is approximately 160 kP.

[0051] Referring to the drawings in general and to Figures 1-3 in particular, it will be understood that the illustrations are for the purpose of describing particular embodiments and are not intended to limit the disclosure or appended claims thereto. The drawings are not necessarily to scale, and certain features and certain views of the drawings may be shown exaggerated in scale or in schematic in the interest of clarity and conciseness.

[0052] As used herein, DOC refers to the depth at which the stress within the glass-based article changes compressive to tensile stress. At the DOC, the stress crosses from a positive (compressive) stress to a negative (tensile) stress (e.g., 130 in Figure 1) and thus exhibits a stress value of zero.

[0053] As used herein, the terms "chemical depth", "chemical depth of layer" and "depth of chemical layer" may be used interchangeably and refer to the depth at which an ion of the metal oxide or alkali metal oxide (e.g., the metal ion or alkali metal ion) diffuses into the glass-based article and the depth at which the concentration of the ion reaches a minimum value, as determined by Electron Probe Micro-Analysis (EPMA) or Glow Discharge - Optival Emission Spectroscopy (GD-OES)). In particular, to assess the depth of Na_2O diffusion or Na+ ion concentration may be determined using EPMA and a surface stress meter (described in more detail below).

[0054] According to the convention normally used in the art, compression is expressed as a negative (< 0) stress and tension is expressed as a positive (> 0) stress. Throughout this description, however, CS is expressed as a positive or absolute value – i.e., as recited herein, $CS = |CS|$.

[0055] Described herein are thin, chemically strengthened glass-based articles that include glasses, such as silicate glasses including alkali-containing glass, and glass-ceramics that may be used as a cover glass for mobile electronic devices and touch-enabled displays. The glass-based articles may also be used in displays (or as display articles) (e.g., billboards, point of sale systems, computers, navigation systems, and the like), architectural articles (walls, fixtures, panels, windows, etc.), transportation articles (e.g., in automotive applications, trains, aircraft, sea craft, etc.), appliances (e.g., washers, dryers, dishwashers, refrigerators and the like), or any article that requires some fracture resistance.

[0056] In particular, the glass-based articles described herein are thin and exhibit stress profiles that are typically only achievable through tempering thick glass articles (e.g., having a thickness of about 2 mm or 3 mm or greater). The glass-based articles exhibit unique stress profiles along the thickness thereof. In some cases, the glass-based articles described herein exhibit a greater surface CS than tempered glass articles. In one or more embodiments, the glass-based articles have a compressive stress layer that extends deeper into the glass-based article (in which the CS decreases and increases more gradually than known chemically strengthened glass-based articles) such the glass-based article exhibits substantially improved fracture resistance, even when the glass-based article or a device including the same is

dropped on a hard surface (e.g., granite) or a hard and rough surface (e.g., asphalt). The glass-based articles of one or more embodiments exhibit a greater maximum CT value than some known chemically strengthened glass substrates.

[0057] CS and depth of compressive stress layer ("DOL") are measured using those means known in the art. DOL is distinguished from DOC by measurement technique in that DOL is determined by surface stress meter using commercially available instruments such as the FSM-6000, manufactured by Luceo Co., Ltd. (Tokyo, Japan), or the like, and methods of measuring CS and depth of layer are described in ASTM 1422C-99, entitled "Standard Specification for Chemically Strengthened Flat Glass," and ASTM 1279.19779 "Standard Test Method for Non-Destructive Photoelastic Measurement of Edge and Surface Stresses in Annealed, Heat-Strengthened, and Fully-Tempered Flat Glass," the contents of which are incorporated herein by reference in their entirety. This technique is commonly referred to as the FSM technique. Surface stress measurements rely upon the accurate measurement of the stress optical coefficient (SOC), which is related to the birefringence of the glass. SOC in turn is measured by those methods that are known in the art, such as fiber and four point bend methods, both of which are described in ASTM standard C770-98 (2008), entitled "Standard Test Method for Measurement of Glass Stress-Optical Coefficient," the contents of which are incorporated herein by reference in their entirety, and a bulk cylinder method.

[0058] For strengthened glass-based articles in which the CS layers extend to deeper depths within the glass-based article, the FSM technique may suffer from contrast issues which affect the observed or measured DOL value. At deeper DOL values, there may be inadequate contrast between the TE and TM spectra, thus making the calculation of the difference between TE and TM spectra – and determining the DOL – more difficult. Moreover, the FSM technique is incapable of determining the stress profile (i.e., the variation of CS as a function of depth within the glass-based article). In addition, the FSM technique is incapable of determining the DOL resulting from the ion exchange of certain elements such as, for example, sodium for lithium.

[0059] The techniques described below have been developed to yield more accurately determine the DOC and stress profiles for strengthened glass-based articles.

[0060] In U.S. Patent Application No. 13/463,322, entitled "Systems And Methods for Measuring the Stress Profile of Ion-Exchanged Glass(hereinafter referred to as "Roussev I")," filed by Rostislav V. Roussev et al. on May 3, 2012, and claiming priority to U.S. Provisional Patent Application No. 61/489,800, having the same title and filed on May 25, 2011, two methods for extracting detailed and precise stress profiles (stress as a function of depth) of

tempered or chemically strengthened glass are disclosed. The spectra of bound optical modes for TM and TE polarization are collected via prism coupling techniques, and used in their entirety to obtain detailed and precise TM and TE refractive index profiles $n_{TM}(z)$ and $n_{TE}(z)$. The contents of the above applications are incorporated herein by reference in their entirety.

[0061] In one embodiment, the detailed index profiles are obtained from the mode spectra by using the inverse Wentzel–Kramers–Brillouin (IWKB) method.

[0062] In another embodiment, the detailed index profiles are obtained by fitting the measured mode spectra to numerically calculated spectra of pre-defined functional forms that describe the shapes of the index profiles and obtaining the parameters of the functional forms from the best fit. The detailed stress profile S(z) is calculated from the difference of the recovered TM and TE index profiles by using a known value of the stress-optic coefficient (SOC):

$$S(z) = [n_{TM}(z) - n_{TE}(z)]/SOC \quad (2).$$

[0063] Due to the small value of the SOC, the birefringence $n_{TM}(z) - n_{TE}(z)$ at any depth z is a small fraction (typically on the order of 1%) of either of the indices $n_{TM}(z)$ and $n_{TE}(z)$. Obtaining stress profiles that are not significantly distorted due to noise in the measured mode spectra requires determination of the mode effective indices with precision on the order of 0.00001 RIU. The methods disclosed in Roussev I further include techniques applied to the raw data to ensure such high precision for the measured mode indices, despite noise and/or poor contrast in the collected TE and TM mode spectra or images of the mode spectra. Such techniques include noise-averaging, filtering, and curve fitting to find the positions of the extremes corresponding to the modes with sub-pixel resolution.

[0064] Similarly, U.S. Patent Application No. 14/033,954, entitled “Systems and Methods for Measuring Birefringence in Glass and Glass-Ceramics (hereinafter “Roussev II”),” filed by Rostislav V. Roussev et al. on September 23, 2013, and claiming priority to U.S. Provisional Application Serial No. 61/706,891, having the same title and filed on September 28, 2012, discloses apparatus and methods for optically measuring birefringence on the surface of glass and glass ceramics, including opaque glass and glass ceramics. Unlike Roussev I, in which discrete spectra of modes are identified, the methods disclosed in Roussev II rely on careful analysis of the angular intensity distribution for TM and TE light reflected by a prism-sample interface in a prism-coupling configuration of measurements. The contents of the above applications are incorporated herein by reference in their entirety.

[0065] Hence, correct distribution of the reflected optical intensity vs. angle is much more important than in traditional prism-coupling stress-measurements, where only the locations of the discrete modes are sought. To this end, the methods disclosed in Roussev 1 and Roussev II comprise techniques for normalizing the intensity spectra, including normalizing to a reference image or signal, correction for nonlinearity of the detector, averaging multiple images to reduce image noise and speckle, and application of digital filtering to further smoothen the intensity angular spectra. In addition, one method includes formation of a contrast signal, which is additionally normalized to correct for fundamental differences in shape between TM and TE signals. The aforementioned method relies on achieving two signals that are nearly identical and determining their mutual displacement with sub-pixel resolution by comparing portions of the signals containing the steepest regions. The birefringence is proportional to the mutual displacement, with a coefficient determined by the apparatus design, including prism geometry and index, focal length of the lens, and pixel spacing on the sensor. The stress is determined by multiplying the measured birefringence by a known stress-optic coefficient.

[0066] In another disclosed method, derivatives of the TM and TE signals are determined after application of some combination of the aforementioned signal conditioning techniques. The locations of the maximum derivatives of the TM and TE signals are obtained with sub-pixel resolution, and the birefringence is proportional to the spacing of the above two maxima, with a coefficient determined as before by the apparatus parameters.

[0067] Associated with the requirement for correct intensity extraction, the apparatus comprises several enhancements, such as using a light-scattering surface (static diffuser) in close proximity to or on the prism entrance surface to improve the angular uniformity of illumination, a moving diffuser for speckle reduction when the light source is coherent or partially coherent, and light-absorbing coatings on portions of the input and output facets of the prism and on the side facets of the prism, to reduce parasitic background which tends to distort the intensity signal. In addition, the apparatus may include an infrared light source to enable measurement of opaque materials.

[0068] Furthermore, Roussev II discloses a range of wavelengths and attenuation coefficients of the studied sample, where measurements are enabled by the described methods and apparatus enhancements. The range is defined by $\alpha_s\lambda < 250\pi\sigma_s$, where α_s is the optical attenuation coefficient at measurement wavelength λ, and σ_s is the expected value of the stress to be measured with typically required precision for practical applications. This wide range allows measurements of practical importance to be obtained at wavelengths where

the large optical attenuation renders previously existing measurement methods inapplicable. For example, Roussev II discloses successful measurements of stress-induced birefringence of opaque white glass-ceramic at a wavelength of 1550 nm, where the attenuation is greater than about 30 dB/mm.

[0069] While it is noted above that there are some issues with the FSM technique at deeper DOL values, FSM is still a beneficial conventional technique which may utilized with the understanding that an error range of up to +/-20% is possible at deeper DOL values. DOL as used herein refers to depths of the compressive stress layer values computed using the FSM technique, whereas DOC refer to depths of the compressive stress layer determined by the methods described in Roussev I & II.

[0070] As stated above, the glass-based articles described herein are chemically strengthened by ion exchange and exhibit stress profiles that are distinguished from those exhibited by known strengthened glass articles. In this disclosure glass-based substrates are generally unstrengthened and glass-based articles generally refer to glass-based substrates that have been strengthened (by, for example, ion exchange). In this process, ions at or near the surface of the glass-based article are replaced by – or exchanged with – larger ions having the same valence or oxidation state. In those embodiments in which the glass-based article comprises an alkali aluminosilicate glass, ions in the surface layer of the glass and the larger ions are monovalent alkali metal cations, such as Li^+ (when present in the glass-based article), Na^+, K^+, Rb^+, and Cs^+. Alternatively, monovalent cations in the surface layer may be replaced with monovalent cations other than alkali metal cations, such as Ag^+ or the like.

[0071] Ion exchange processes are typically carried out by immersing a glass-based substrate in a molten salt bath (or two or more molten salt baths) containing the larger ions to be exchanged with the smaller ions in the glass-based substrate. It should be noted that aqueous salt baths may also be utilized. In addition, the composition of the bath(s) may include more than one type of larger ion (e.g., Na+ and K+) or a single larger ion. It will be appreciated by those skilled in the art that parameters for the ion exchange process, including, but not limited to, bath composition and temperature, immersion time, the number of immersions of the glass-based article in a salt bath (or baths), use of multiple salt baths, additional steps such as annealing, washing, and the like, are generally determined by the composition of the glass-based article (including the structure of the article and any crystalline phases present) and the desired DOL or DOC and CS of the glass-based article that results from strengthening. By way of example, ion exchange of glass-based substrates may be achieved by immersion of the glass-based substrates in at least one molten bath

containing a salt such as, but not limited to, nitrates, sulfates, and chlorides of the larger alkali metal ion. Typical nitrates include KNO_3, $NaNO_3$, $LiNO_3$, $NaSO_4$ and combinations thereof. The temperature of the molten salt bath typically is in a range from about 380ºC up to about 450ºC, while immersion times range from about 15 minutes up to about 100 hours depending on glass thickness, bath temperature and glass diffusivity. However, temperatures and immersion times different from those described above may also be used.

[0072] In one or more embodiments, the glass-based substrates may be immersed in a molten salt bath of 100% $NaNO_3$ having a temperature from about 370 °C to about 480 °C. In some embodiments, the glass-based substrate may be immersed in a molten mixed salt bath including from about 5% to about 90% KNO_3 and from about 10% to about 95% $NaNO_3$. In some embodiments, the glass-based substrate may be immersed in a molten mixed salt bath including Na_2SO_4 and $NaNO_3$ and have a wider temperature range (e.g., up to about 500 °C). In one or more embodiments, the glass-based article may be immersed in a second bath, after immersion in a first bath. Immersion in a second bath may include immersion in a molten salt bath including 100% KNO_3 for 15 minutes to 8 hours.

[0073] In one or more embodiments, the glass-based substrate may be immersed in a molten, mixed salt bath including $NaNO_3$ and KNO_3 (e.g., 49%/51%, 50%/50%, 51%/49%) having a temperature less than about 420 °C (e.g., about 400 °C or about 380 °C). for less than about 5 hours, or even about 4 hours or less.

[0074] Ion exchange conditions can be tailored to provide a "spike" or to increase the slope of the stress profile at or near the surface of the resulting glass-based article. This spike can be achieved by single bath or multiple baths, with the bath(s) having a single composition or mixed composition, due to the unique properties of the glass compositions used in the glass-based articles described herein.

[0075] As illustrated in Figure 3, the glass-based article 300 of one or more embodiments includes a first surface 302 and a second surface 304 opposing the first surface, defining a thickness *t*. In one or more embodiments, the thickness *t* may be about 3 millimeters or less (e.g., in the range from about 0.01 millimeter to about 3 millimeters, from about 0.1 millimeter to about 3 millimeters, from about 0.2 millimeter to about 3 millimeters, from about 0.3 millimeter to about 3 millimeters, from about 0.4 millimeter to about 3 millimeters, from about 0.01 millimeter to about 2.5 millimeters, from about 0.01 millimeter to about 2 millimeters, from about 0.01 millimeter to about 1.5 millimeters, from about 0.01 millimeter to about 1 millimeter, from about 0.01 millimeter to about 0.9 millimeter, from about 0.01 millimeter to about 0.8 millimeter, from about 0.01 millimeter to about 0.7 millimeter, from

about 0.01 millimeter to about 0.6 millimeter, from about 0.01 millimeter to about 0.5 millimeter, from about 0.1 millimeter to about 0.5 millimeter, or from about 0.3 millimeter to about 0.5 millimeter.)

[0076] The glass-based article includes a stress profile that extends from the first surface 302 to the second surface 304 (or along the entire length of the thickness *t*). In the embodiment shown in Figure 3, the stress profile 312 as measured by Roussev I & II as described herein is shown along with the stress profile 340 estimated by FSM techniques as described herein. The x-axis represents the stress value and the y-axis represents the thickness or depth within the glass-based article.

[0077] As illustrated in Figure 3, the stress profile 312 includes a CS layer 315 (with a surface CS 310), a CT layer 325 (with a maximum CT 320) and a DOC 317 at which the stress profile 312 turns from compressive to tensile at 330. The CT layer 325 also has an associated depth or length 327 (CT region or layer). The estimated stress profile 340 includes a DOL that is greater than the DOC. As used herein, reference to the DOC and DOL is with respect to a depth from one surface (either the first surface 302 or the second surface 304), with the understanding that such DOC or DOL may also be present from the other surface.

[0078] The surface CS 310 may be about 150 MPa or greater or about 200 MPa or greater (e.g., about 250 MPa or greater, about 300 MPa or greater, about 400 MPa or greater, about 450 MPa or greater, about 500 MPa or greater, or about 550 MPa or greater). The surface CS 310 may be up to about 900 MPa, up to about 1000 MPa, up to about 1100 MPa, or up to about 1200 MPa. The surface CS values provided herein may also comprise the maximum CS. In some embodiments, the surface CS is less than the maximum CS.

[0079] The maximum CT 320 may be about 80 MPa or less, about 75 MPa or less, or about 70 MPa or less (e.g., about 60 MPa or less, about 55 MPa or less, 50 MPa or less, or about 40 MPa or less). In some embodiments, the maximum CT 320 may be in the range from about 25 MPa to about 80 MPa (e.g., from about 25 MPa to about 75 MPa, from about 25 MPa to about 70 MPa, from about 25 MPa to about 65 MPa, from about 45 MPa to about 80 MPa, from about 50 MPa to about 80 MPa, or from about 60 MPa to about 80 MPa).

[0080] The maximum CT 320 may be positioned at a range from about $0.3\bullet t$ to about $0.7\bullet t$, from about $0.4\bullet t$ to about $0.6\bullet t$ or from about $0.45\bullet t$ to about $0.55\bullet t$. It should be noted that any one or more of surface CS 310 and maximum CT 320 may be dependent on the thickness of the glass-based article. For example, glass-based articles having at thickness of about 0.8 mm may have a maximum CT of about 75 MPa or less. When the thickness of the glass-

based article decreases, the maximum CT may increase. In other words, the maximum CT increases with decreasing thickness (or as the glass-based article becomes thinner).

[0081] In some embodiments, the ratio of the maximum CT 320 to the surface CS 310 in the range from about 0.01 to about 0.2 (e.g., in the range from about 0.01 to about 0.18, from about 0.01 to about 0.16, from about 0.01 to about 0.15, from about 0.01 to about 0.14, from about 0.01 to about 0.1, from about 0.02 to about 0.2, from about 0.04 to about 0.2, from about 0.05 to about 0.2, from about 0.06 to about 0.2, from about 0.08 to about 0.2, from about 0.1 to about 0.2, or from about 0.12 to about 0.2). In known chemically strengthened glass-based articles, the ratio of the maximum CT 320 to the surface CS 310 is 0.2 or less, or about 0.15 or less. In some embodiments, surface CS may be 1.5 times (or 2 times or 2.5 times) the maximum CT or greater. In some embodiments, the surface CS may be up to about 48 times the maximum CT, up to 40 times the maximum CT, up to 20 times the maximum CT, 10 up to times the maximum CT, or up to 8 times the maximum CT. The surface CS may be in the range from about 5 times up to about 50 times the maximum CT.

[0082] In one or more embodiments, the stress profile 312 comprises a maximum CS, which is typically the surface CS 310 and can be found at one or both of the first surface 302 and the second surface 304. In one or more embodiments, the CS layer or region 315 extends along a portion of the thickness to the DOC 317 and a maximum CT 320. In one or more embodiments, the DOC 317 may be about 0.1•*t* or greater. For example, the DOC 317 may be about 0.12•*t* or greater, about 0.14•*t* or greater, about 0.15•*t* or greater, about 0.16•*t* or greater, 0.17•*t* or greater, 0.18•*t* or greater, 0.19•*t* or greater, 0.20•*t* or greater, about 0.21•*t* or greater, or up to about 0.25•*t*. In some embodiments, the DOC 317 is less than the chemical depth 342. The chemical depth 342 may be about 0.4•*t* or greater, 0.5•*t* or greater, about 55•*t* or greater, or about 0.6•*t* or greater. In one or more embodiments, the stress profile 312 may be described as parabolic-like in shape. In some embodiments, the stress profile along the region or depth of the glass-based article exhibiting tensile stress exhibits a parabolic-like shape. In one or more specific embodiments, the stress profile 312 is free of a flat stress (i.e., compressive or tensile) portion or a portion that exhibits a substantially constant stress (i.e., compressive or tensile). In some embodiments, the CT region exhibits a stress profile that is substantially free of a flat stress or free of a substantially constant stress. In one or more embodiments, all points of the stress profile 312 between a thickness range from about 0*t* up to about 0.2•*t* and greater than 0.8•*t* (or from about 0•*t* to about 0.3•*t* and greater than 0.7•*t*) comprise a tangent that is less than about -0.1 MPa/micrometers or greater than about 0.1 MPa/micrometers. In some embodiments, the tangent may be less than about -0.2

MPa/micrometers or greater than about 0.2 MPa/micrometers. In some more specific embodiments, the tangent may be less than about -0.3 MPa/micrometers or greater than about 0.3 MPa/micrometers. In even more specific embodiments, the tangent may be less than about -0.5 MPa/micrometers or greater than about 0.5 MPa/micrometers. In other words, the stress profile of one or more embodiments along these thickness ranges (i.e., 0•*t* up to about 2•*t* and greater than 0.8*t*, or from about 0*t* to about 0.3•*t* and 0.7•*t* or greater) exclude points having a tangent, as described herein. Without being bound by theory, known error function or quasi-linear stress profiles have points along these thickness ranges (i.e., from about 0•*t* up to about 2•*t* and greater than 0.8•*t*, or from about 0•*t* to about 0.3•*t* and 0.7•*t* or greater) that have a tangent that is in the range from about -0.1 MPa/micrometers to about 0.1 MPa/micrometers, from about -0.2 MPa/micrometers to about 0.2 MPa/micrometers, from about -0.3 MPa/micrometers to about 0.3 MPa/micrometers, or from about -0.5 MPa/micrometers to about 0.5 MPa/micrometers (indicating a flat or zero slope stress profile along such thickness ranges, as shown in Figure 2, 220). The glass-based articles of one or more embodiments of this disclosure do not exhibit such a stress profile having a flat or zero slope stress profile along these thickness ranges, as shown in Figure 3.

[0083] In one or more embodiments, the glass-based article exhibits a stress profile in a thickness range from about 0.1•*t* to 0.3•*t* and from about 0.7•*t* to 0.9•*t* that comprises a maximum tangent and a minimum tangent. In some instances, the difference between the maximum tangent and the minimum tangent is about 3.5 MPa/micrometers or less, about 3 MPa/micrometers or less, about 2.5 MPa/micrometers or less, or about 2 MPa/micrometers or less.

[0084] In one or more embodiments, the glass-based article includes a stress profile 312 that is substantially free of any linear segments that extend in a depth direction or along at least a portion of the thickness *t* of the glass-based article. In other words, the stress profile 312 is substantially continuously increasing or decreasing along the thickness *t*. In some embodiments, the stress profile is substantially free of any linear segments in a depth direction having a length of about 10 micrometers or more, about 50 micrometers or more, or about 100 micrometers or more, or about 200 micrometers or more. As used herein, the term “linear” refers to a slope having a magnitude of less than about 5 MPa/micrometer, or less than about 2 MPa/micrometer along the linear segment. In some embodiments, one or more portions of the stress profile that are substantially free of any linear segments in a depth direction are present at depths within the glass-based article of about 5 micrometers or greater (e.g., 10 micrometers or greater, or 15 micrometers or greater) from either one or both the

first surface or the second surface. For example, along a depth of about 0 micrometers to less than about 5 micrometers from the first surface, the stress profile may include linear segments, but from a depth of about 5 micrometers or greater from the first surface, the stress profile may be substantially free of linear segments.

[0085] In some embodiments, the stress profile may include linear segments at depths from about $0t$ up to about $0.1t$ and may be substantially free of linear segments at depths of about $0.1t$ to about $0.4t$. In some embodiments, the stress profile from a thickness in the range from about $0t$ to about $0.1t$ may have a slope in the range from about 20 MPa/microns to about 200 MPa/microns. As will be described herein, such embodiments may be formed using a single ion-exchange process by which the bath includes two or more alkali salts or is a mixed alkali salt bath or multiple (e.g., 2 or more) ion exchange processes.

[0086] In one or more embodiments, the glass-based article may be described in terms of the shape of the stress profile along the CT region (327 in Figure 3). For example, in some embodiments, the stress profile along the CT region (where stress is in tension) may be approximated by equation. In some embodiments, the stress profile along the CT region may be approximated by equation (1):

$$\text{Stress}(x) = \text{MaxCT} - (((\text{MaxCT} \bullet (n+1))/0.5^n)\bullet|(x/t)-0.5|^n) \qquad (1)$$

In equation (1), the stress (x) is the stress value at position x. Here the stress is positive (tension). MaxCT is the maximum central tension as a positive value in MPa. The value x is position along the thickness (t) in micrometers, with a range from 0 to t; x=0 is one surface (302, in Figure 3), x=0.5t is the center of the glass-based article, stress(x)=MaxCT, and x=t is the opposite surface (304, in Figure 3). MaxCT used in equation (1) may be in the range from about 50 MPa to about 80 MPa (e.g., from about 60 MPa to about 80 MPa, from about 70 MPa to about 80 MPa, from about 50 MPa to about 75 MPa, from about 50 MPa to about 70 MPa, or from about 50 MPa to about 65 MPa), and n is a fitting parameter from 1.5 to 5 (e.g., 2 to 4, 2 to 3 or 1.8 to 2.2) whereby n=2 can provide a parabolic stress profile, exponents that deviate from n=2 provide stress profiles with near parabolic stress profiles.

[0087] In some embodiments, the stress profile may be modified by heat treatment. In such embodiments, the heat treatment may occur before any ion-exchange processes, between ion-exchange processes, or after all ion-exchange processes. In some embodiments, the heat treatment may result reduce the slope of the stress profile at or near the surface. In some embodiments, where a steeper or greater slope is desired at the surface, an ion-exchange process after the heat treatment may be utilized to provide a “spike” or to increase the slope of the stress profile at or near the surface.

[0088] In one or more embodiments, the stress profile 312 (and/or estimated stress profile 340) is generated due to a non-zero concentration of a metal oxide(s) that varies along a portion of the thickness. The variation in concentration may be referred to herein as a gradient. In some embodiments, the concentration of a metal oxide is non-zero and varies, both along a thickness range from about 0•*t* to about 0.3•*t*. In some embodiments, the concentration of the metal oxide is non-zero and varies along a thickness range from about 0•*t* to about 0.35•*t*, from about 0•*t* to about 0.4•*t*, from about 0•*t* to about 0.45•*t* or from about 0•*t* to about 0.48•*t*. The metal oxide may be described as generating a stress in the glass-based article. The variation in concentration may be continuous along the above-referenced thickness ranges. Variation in concentration may include a change in metal oxide concentration of about 0.2 mol% along a thickness segment of about 100 micrometers. This change may be measured by known methods in the art including microprobe, as shown in Example 1. The metal oxide that is non-zero in concentration and varies along a portion of the thickness may be described as generating a stress in the glass-based article.

[0089] The variation in concentration may be continuous along the above-referenced thickness ranges. In some embodiments, the variation in concentration may be continuous along thickness segments in the range from about 10 micrometers to about 30 micrometers. In some embodiments, the concentration of the metal oxide decreases from the first surface to a point between the first surface and the second surface and increases from the point to the second surface.

[0090] The concentration of metal oxide may include more than one metal oxide (e.g., a combination of Na_2O and K_2O). In some embodiments, where two metal oxides are utilized and where the radius of the ions differ from one or another, the concentration of ions having a larger radius is greater than the concentration of ions having a smaller radius at shallow depths, while the at deeper depths, the concentration of ions having a smaller radius is greater than the concentration of ions having larger radius. For example, where a single Na- and K-containing bath is used in the ion exchange process, the concentration of K+ ions in the glass-based article is greater than the concentration of Na+ ions at shallower depths, while the concentration of Na+ is greater than the concentration of K+ ions at deeper depths. This is due, in part, due to the size of the ions. In such glass-based articles, the area at or near the surface comprises a greater CS due to the greater amount of larger ions (i.e., K+ ions) at or near the surface. This greater CS may be exhibited by a stress profile having a steeper slope at or near the surface (i.e., a spike in the stress profile at the surface).

[0091] The concentration gradient or variation of one or more metal oxides is created by chemically strengthening a glass-based substrate, as previously described herein, in which a plurality of first metal ions in the glass-based substrate is exchanged with a plurality of second metal ions. The first ions may be ions of lithium, sodium, potassium, and rubidium. The second metal ions may be ions of one of sodium, potassium, rubidium, and cesium, with the proviso that the second alkali metal ion has an ionic radius greater than the ionic radius than the first alkali metal ion. The second metal ion is present in the glass-based substrate as an oxide thereof (e.g., Na_2O, K_2O, Rb_2O, Cs_2O or a combination thereof).

[0092] In one or more embodiments, the metal oxide concentration gradient extends through a substantial portion of the thickness *t* or the entire thickness *t* of the glass-based article, including the CT layer 327. In one or more embodiments, the concentration of the metal oxide is about 0.5 mol% or greater in the CT layer 327. In some embodiments, the concentration of the metal oxide may be about 0.5 mol% or greater (e.g., about 1 mol% or greater) along the entire thickness of the glass-based article, and is greatest at the first surface 302 and/or the second surface 304 and decreases substantially constantly to a point between the first surface 302 and the second surface 304. At that point, the concentration of the metal oxide is the least along the entire thickness *t*; however the concentration is also non-zero at that point. In other words, the non-zero concentration of that particular metal oxide extends along a substantial portion of the thickness *t* (as described herein) or the entire thickness *t*. In some embodiments, the lowest concentration in the particular metal oxide is in the CT layer 327. The total concentration of the particular metal oxide in the glass-based article may be in the range from about 1 mol% to about 20 mol%.

[0093] In one or more embodiments, the glass-based article includes a first metal oxide concentration and a second metal oxide concentration, such that the first metal oxide concentration is in the range from about 0 mol% to about 15 mol% along a first thickness range from about 0t to about 0.5t, and the second metal oxide concentration is in the range from about 0 mol% to about 10 mol% from a second thickness range from about 0 micrometers to about 25 micrometers (or from about 0 micrometers to about 12 micrometers); however, the concentration of one or both the first metal oxide and the second metal oxide is non-zero along a substantial portion or the entire thickness of the glass-based article. The glass-based article may include an optional third metal oxide concentration. The first metal oxide may include Na_2O while the second metal oxide may include K_2O.

[0094] The concentration of the metal oxide may be determined from a baseline amount of the metal oxide in the glass-based article prior to being modified to include the concentration gradient of such metal oxide.

[0095] In one or more embodiments, the glass-based articles may be described in terms of how they fracture and the fragments that result from such fracture. In one or more embodiments, when fractured, the glass-based articles fracture into 2 or more fragments per square inch (or per 6.4516 square centimeters) of the glass-based article (prior to fracture). In some cases, the glass-based articles fracture into 3 or more, 4 or more, 5 or more, or 10 or more fragments per square inch (or per 6.4516 square centimeters) of the glass-based article (prior to fracture). In some instances, when fractured, the glass-based articles fracture into fragments such that 50% or more of the fragments have a surface area that is less than 5%, less than 2%, or less than 1% of the surface area of the glass-based article (prior to fracture). In some embodiments, when fractured, the glass-based articles fracture into fragments such that 90% or more or even 100% of the fragments have a surface area that is less than 5%, less than 2%, or less than 1% of the surface area of the glass-based article (prior to fracture).

[0096] In one or more embodiments, after chemically strengthening the glass-based article, the resulting stress profile 317 (and estimated stress profile 340) of the glass-based article provides improved fracture resistance. For example, in some embodiments, upon fracture, the glass-based article comprises fragments having an average longest cross-sectional dimension of less than or equal to about 2•*t* (e.g., 1.8•*t*, 1.6•*t*, 1.5•*t*, 1.4•*t*, 1.2•*t* or 1.•*t* or less).

[0097] In one or more embodiments, the glass-based articles may exhibit a fracture toughness (K_{1C}) of about 0.7 MPa·m$^{1/2}$ or greater. In some cases, the fracture toughness may be about 0.8 MPa·m$^{1/2}$ or greater, or about 0.9 MPa·m$^{1/2}$ or greater. In some embodiments the fracture toughness may be in the range from about 0.7 MPa·m$^{1/2}$ to about 1 MPa·m$^{1/2}$.

[0098] In some embodiments, the substrate may also be characterized as having a hardness from about 500 HVN to about 800 HVN, as measured by Vickers hardness test at a load of 200 g.

[0099] The glass-based articles described herein may exhibit a stored tensile energy in the range from greater than 0 J/m^2 to about 20 J/m^2. In some instances, the stored tensile energy may be in the range from about 1 J/m^2 to about 20 J/m^2, from about 2 J/m^2 to about 20 J/m^2, from about 3 J/m^2 to about 20 J/m^2, from about 4 J/m^2 to about 20 J/m^2, from about 1 J/m^2 to about 19 J/m^2, from about 1 J/m^2 to about 18 J/m^2, from about 1 J/m^2 to about 16 J/m^2, from about 4 J/m^2 to about 20 J/m^2, or from about 4 J/m^2 to about 18 J/m^2. The stored tensile

energy is calculated by integrating in the tensile region the stored elastic energy Σ per unit area of specimen of thickness *t* using Equation (2):

$$\Sigma=0.5\sigma^2 t/E \qquad (2)$$

in which σ is stress and E is young's modulus.

[00100] More specifically, stored tensile energy is calculated using the following Equation (3):

$$\text{stored tensile energy } (J/m^2) = 1\text{-}\nu/2E \int\sigma\text{^}2dt \qquad (3)$$

where n is Poisson's ratio, E is the elastic modulus and the integration is computed for the tensile region only.

[00101] The glass–based articles described herein generally have elastic modulus or Young's modulus of less than about 80 GPa. The elastic modulus, which is intrinsic to the composition of the glass-based article, can provide the desired high stiffness, which is an extrinsic property, to the ultimate glass-based article that is produced therefrom. For clarity, unless the specific type of elastic modulus measurement is explicitly indicated, the elastic modulus described herein will be the Young's modulus of a material, rather than, for example, shear modulus, bulk modulus, Poisson's ratio, and the like.

[00102] In some embodiments, the glass-based article comprises a high liquidus viscosity that enables the formation of the glass-based articles via down-draw techniques (e.g., fusion draw, slot draw, and other like methods), which can provide high precision surface smoothness. As used herein, the term "liquidus viscosity" refers to the viscosity of a molten glass at the liquidus temperature, wherein the term "liquidus temperature" refers to the temperature at which crystals first appear as a molten glass cools down from the melting temperature (or the temperature at which the very last crystals melt away as temperature is increased from room temperature). In general, the glass-based articles (or the compositions used to form such articles) described herein a liquidus viscosity of about 100 kilopoise (kP) or greater. In scenarios where a higher liquidus viscosity is desired for down-draw processability, the glass-based articles (or the compositions used to form such articles) exhibit a liquidus viscosity of at least about 200 kP (e.g., about 600 kP or greater).

[00103] In one or more embodiments, the glass-based articles exhibit a Knoop Lateral Cracking Scratch Threshold in the range from about 4 N to about 7 N, from about 4.5 N to about 7 N, from about 5 N to about 7 N, from about 4 N to about 6.5 N, from about 4 N to about 6 N, or from about 5 N to about 6 N. As used herein, Knoop Scratch Lateral Cracking Threshold is the onset of lateral cracking (in 3 or more of 5 indentation events) which extend

equal to or greater than 2 times the width of the microductile scratch groove, formed using a Knoop indenter.

[00104] In one or more embodiments, the glass-based articles exhibit a Vickers Indentation Fracture Threshold in the range from about 10 kgf or greater, about 12 kgf or greater, or about 15 kgf or greater. As used herein, Vickers Indentation Fracture Threshold is the onset of median/radial cracking (in 3 or more of 5 indentation events) extending from at least one corner of the indentation site.

[00105] In one or more embodiments, the glass-based articles exhibit improved surface strength when subjected to abraded ring-on-ring (AROR) testing. The strength of a material is defined as the stress at which fracture occurs. The AROR test is a surface strength measurement for testing flat glass specimens, and ASTM C1499-09(2013), entitled "Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature," serves as the basis for the AROR test methodology described herein. The contents of ASTM C1499-09 are incorporated herein by reference in their entirety. In one embodiment, the glass specimen is abraded prior to ring-on-ring testing with 90 grit silicon carbide (SiC) particles that are delivered to the glass sample using the method and apparatus described in Annex A2, entitled "abrasion Procedures," of ASTM C158-02(2012), entitled "Standard Test Methods for Strength of Glass by Flexure (Determination of Modulus of Rupture). The contents of ASTM C158-02 and the contents of Annex 2 in particular are incorporated herein by reference in their entirety.

[00106] Prior to ring-on-ring testing a surface of the glass-based article is abraded as described in ASTM C158-02, Annex 2, to normalize and/or control the surface defect condition of the sample using the apparatus shown in Figure A2.1 of ASTM C158-02. The abrasive material is typically sandblasted onto the surface 110 of the glass-based article at a load of 15 psi using an air pressure of 304 kPa (44 psi); although in the Examples below, the abrasive material was sandblasted onto the surface 110 at other loads (e.g., 25 psi or 45 psi). After air flow is established, 5 cm^3 of abrasive material is dumped into a funnel and the sample is sandblasted for 5 seconds after introduction of the abrasive material.

[00107] For the AROR test, a glass-based article having at least one abraded surface 410 as shown in Figure 4 is placed between two concentric rings of differing size to determine equibiaxial flexural strength (i.e., the maximum stress that a material is capable of sustaining when subjected to flexure between two concentric rings), as also shown in FIG. 4. In the AROR configuration 400, the abraded glass-based article 410 is supported by a support ring

420 having a diameter D2. A force F is applied by a load cell (not shown) to the surface of the glass-based article by a loading ring 430 having a diameter D1.

[00108] The ratio of diameters of the loading ring and support ring D1/D2 may be in a range from about 0.2 to about 0.5. In some embodiments, D1/D2 is about 0.5. Loading and support rings 130, 120 should be aligned concentrically to within 0.5% of support ring diameter D2. The load cell used for testing should be accurate to within ±1% at any load within a selected range. In some embodiments, testing is carried out at a temperature of 23±2°C and a relative humidity of 40±10%.

[00109] For fixture design, the radius r of the protruding surface of the loading ring 430, $h/2 \leq r \leq 3h/2$, where h is the thickness of glass-based article 410. Loading and support rings 430, 420 are typically made of hardened steel with hardness HRc > 40. AROR fixtures are commercially available.

[00110] The intended failure mechanism for the AROR test is to observe fracture of the glass-based article 410 originating from the surface 430a within the loading ring 430. Failures that occur outside of this region – i.e., between the loading rings 430 and support rings 420 – are omitted from data analysis. Due to the thinness and high strength of the glass-based article 410, however, large deflections that exceed ½ of the specimen thickness h are sometimes observed. It is therefore not uncommon to observe a high percentage of failures originating from underneath the loading ring 430. Stress cannot be accurately calculated without knowledge of stress development both inside and under the ring (collected via strain gauge analysis) and the origin of failure in each specimen. AROR testing therefore focuses on peak load at failure as the measured response.

[00111] The strength of glass-based article depends on the presence of surface flaws. However, the likelihood of a flaw of a given size being present cannot be precisely predicted, as the strength of glass is statistical in nature. A probability distribution can therefore generally be used as a statistical representation of the data obtained.

[00112] In some embodiments, the glass-based articles described herein have a surface or equibiaxial flexural strength of at least 20 kgf and up to about 30 kgf as determined by AROR testing using a load of 25 psi or even 45 psi to abrade the surface. In other embodiments, the surface strength is at least 25 kgf, and in still other embodiments, at least 30 kgf.

[00113] In some embodiments, the glass-based articles described herein may be described in terms of performance in an inverted ball on sandpaper (IBoS) test. The IBoS test is a dynamic component level test that mimics the dominant mechanism for failure due to damage

introduction plus bending that typically occurs in glass-based articles that are used in mobile or hand held electronic devices, as schematically shown in Figure 36. In the field, damage introduction (a in Figure 37) occurs on the top surface of the glass-based article. Fracture initiates on the top surface of the glass-based article and damage either penetrates the glass-based article (b in Figure 37) or the fracture propagates from bending on the top surface or from the interior portions of the glass-based article (c in Figure 37). The IBoS test is designed to simultaneously introduce damage to the surface of the glass and apply bending under dynamic load. In some instances, the glass-based article exhibits improved drop performance when it includes a compressive stress than if the same glass-based article does not include a compressive stress.

[00114] An IBoS test apparatus is schematically shown in Figure 36. Apparatus 500 includes a test stand 510 and a ball 530. Ball 530 is a rigid or solid ball such as, for example, a stainless steel ball, or the like. In one embodiment, ball 530 is a 4.2 gram stainless steel ball having diameter of 10 mm. The ball 530 is dropped directly onto the glass-based article sample 518 from a predetermined height **h**. Test stand 510 includes a solid base 512 comprising a hard, rigid material such as granite or the like. A sheet 514 having an abrasive material disposed on a surface is placed on the upper surface of the solid base 512 such that surface with the abrasive material faces upward. In some embodiments, sheet 514 is sandpaper having a 30 grit surface and, in other embodiments, a 180 grit surface. The glass-based article sample 518 is held in place above sheet 514 by sample holder 515 such that an air gap 516 exists between glass-based article sample 518 and sheet 514. The air gap 516 between sheet 514 and glass-based article sample 518 allows the glass-based article sample 518 to bend upon impact by ball 530 and onto the abrasive surface of sheet 514. In one embodiment, the glass-based article sample 218 is clamped across all corners to keep bending contained only to the point of ball impact and to ensure repeatability. In some embodiments, sample holder 514 and test stand 510 are adapted to accommodate sample thicknesses of up to about 2 mm. The air gap 516 is in a range from about 50 μm to about 100 μm. Air gap 516 is adapted to adjust for difference of material stiffness (Young's modulus, Emod), but also includes the elastic modulus and thickness of the sample. An adhesive tape 520 may be used to cover the upper surface of the glass-based article sample to collect fragments in the event of fracture of the glass-based article sample 518 upon impact of ball 530.

[00115] Various materials may be used as the abrasive surface. In a one particular embodiment, the abrasive surface is sandpaper, such as silicon carbide or alumina sandpaper, engineered sandpaper, or any abrasive material known to those skilled in the art for having

comparable hardness and/or sharpness. In some embodiments, sandpaper having 30 grit may be used, as it has a surface topography that is more consistent than either concrete or asphalt, and a particle size and sharpness that produces the desired level of specimen surface damage.

[00116] In one aspect, a method 600 of conducting the IBoS test using the apparatus 500 described hereinabove is shown in Figure 38. In Step 610, a glass-based article sample (218 in Figure 36) is placed in the test stand 510, described previously and secured in sample holder 515 such that an air gap 516 is formed between the glass-based article sample 518 and sheet 514 with an abrasive surface. Method 600 presumes that the sheet 514 with an abrasive surface has already been placed in test stand 510. In some embodiments, however, the method may include placing sheet 514 in test stand 510 such that the surface with abrasive material faces upward. In some embodiments (Step 610a), an adhesive tape 520 is applied to the upper surface of the glass-based article sample 518 prior to securing the glass-based article sample 518 in the sample holder 510.

[00117] In Step 520, a solid ball 530 of predetermined mass and size is dropped from a predetermined height **h** onto the upper surface of the glass-based article sample 518, such that the ball 530 impacts the upper surface (or adhesive tape 520 affixed to the upper surface) at approximately the center (i.e., within 1 mm, or within 3 mm, or within 5 mm, or within 10 mm of the center) of the upper surface. Following impact in Step 520, the extent of damage to the glass-based article sample 518 is determined (Step 630). As previously described hereinabove, herein, the term “fracture” means that a crack propagates across the entire thickness and/or entire surface of a substrate when the substrate is dropped or impacted by an object.

[00118] In method 600, the sheet 518 with the abrasive surface may be replaced after each drop to avoid “aging” effects that have been observed in repeated use of other types (e.g., concrete or asphalt) of drop test surfaces.

[00119] Various predetermined drop heights **h** and increments are typically used in method 600. The test may, for example, utilize a minimum drop height to start (e.g., about 10-20 cm). The height may then be increased for successive drops by either a set increment or variable increments. The test described in method 600 is stopped once the glass-based article sample 518 breaks or fractures (Step 631). Alternatively, if the drop height **h** reaches the maximum drop height (e.g., about 100 cm) without fracture, the drop test of method 300 may also be stopped, or Step 520 may be repeated at the maximum height until fracture occurs.

[00120] In some embodiments, IBoS test of method 600 is performed only once on each glass-based article sample 518 at each predetermined height **h**. In other embodiments, however, each sample may be subjected to multiple tests at each height.

[00121] If fracture of the glass-based article sample 518 has occurred (Step 631 in Figure 38), the IBoS test according to method 600 is ended (Step 640). If no fracture resulting from the ball drop at the predetermined drop height is observed (Step 632), the drop height is increased by a predetermined increment (Step 634) – such as, for example 5, 10, or 20 cm – and Steps 620 and 630 are repeated until either sample fracture is observed (631) or the maximum test height is reached (636) without sample fracture. When either Step 631 or 636 is reached, the test according to method 600 is ended.

[00122] When subjected to the inverted ball on sandpaper (IBoS) test described above, embodiments of the glass-based article described herein have at least about a 60% survival rate when the ball is dropped onto the surface of the glass from a height of 100 cm. For example, a glass-based article is described as having a 60% survival rate when dropped from a given height when three of five identical (or nearly identical) samples (i.e., having approximately the same composition and, when strengthened, approximately the same compressive stress and depth of compression or compressive stress layer, as described herein) survive the IBoS drop test without fracture when dropped from the prescribed height (here 100 cm). In other embodiments, the survival rate in the 100 cm IBoS test of the glass-based articles that are strengthened is at least about 70%, in other embodiments, at least about 80%, and, in still other embodiments, at least about 90%. In other embodiments, the survival rate of the strengthened glass-based articles dropped from a height of 100 cm in the IBoS test is at least about 60%, in other embodiments, at least about 70%, in still other embodiments, at least about 80%, and, in other embodiments, at least about 90%. In one or more embodiments, the survival rate of the strengthened glass-based articles dropped from a height of 150 cm in the IBoS test is at least about 60%, in other embodiments, at least about 70%, in still other embodiments, at least about 80%, and, in other embodiments, at least about 90%.

[00123] To determine the survivability rate of the glass-based articles when dropped from a predetermined height using the IBoS test method and apparatus described hereinabove, at least five identical (or nearly identical) samples (i.e., having approximately the same composition and, if strengthened, approximately the same compressive stress and depth of compression or layer) of the glass-based articles are tested, although larger numbers (e.g., 10, 20, 30, etc.) of samples may be subjected to testing to raise the confidence level of the test results. Each sample is dropped a single time from the predetermined height (e.g., 100 cm or

150 cm) or, alternatively, dropped from progressively higher heights without fracture until the predetermined height is reached, and visually (i.e., with the naked eye) examined for evidence of fracture (crack formation and propagation across the entire thickness and/or entire surface of a sample). A sample is deemed to have "survived" the drop test if no fracture is observed after being dropped from the predetermined height, and a sample is deemed to have "failed (or "not survived") if fracture is observed when the sample is dropped from a height that is less than or equal to the predetermined height. The survivability rate is determined to be the percentage of the sample population that survived the drop test. For example, if 7 samples out of a group of 10 did not fracture when dropped from the predetermined height, the survivability rate of the glass would be 70%.

[00124] The glass-based articles described herein may be transparent. In one or more the glass-based article may have a thickness of about 1 millimeter or less and exhibit a transmittance of about 88% or greater over a wavelength in the range from about 380 nm to about 780 nm.

[00125] The glass-based article may also exhibit a substantially white color. For example, the glass-based article may exhibit CIELAB color space coordinates, under a CIE illuminant F02, of L* values of about 88 and greater, a* values in the range from about -3 to about +3, and b* values in the range from about -6 to about +6.

[00126] Choice of substrates not particularly limited. In some examples, the glass-based article may be described as having a high cation diffusivity for ion exchange. In one or more embodiments, the glass or glass-ceramic has fast ion-exchange capability, i.e., where diffusivity is greater than 500μm^2/hr or may be characterized as greater than 450 μm^2/hour at 460 °C.

[00127] At a certain temperature the diffusivity is calculated using the equation (4):

Diffusivity =DOL^2/5.6*T (4)

in which DOL is depth of ion-exchange layer and T is the IOX time it takes to reach that DOL.

[00128] The glass-based article may include an amorphous substrate, a crystalline substrate or a combination thereof (e.g., a glass-ceramic substrate). In one or more embodiments, the glass-based article substrate (prior to being chemically strengthened as described herein) may include a glass composition, in mole percent (mole%), including:

SiO_2 in the range from about 40 to about 80, Al_2O_3 in the range from about 10 to about 30, B_2O_3 in the range from about 0 to about 10, R_2O in the range from about 0 to about 20, and RO in the range from about 0 to about 15. In some instances, the composition may include

either one or both of ZrO_2 in the range from about 0 mol% to about 5 mol% and P_2O_5 in the range from about 0 to about 15 mol%. TiO2 can be present from about 0 mol% to about 2 mol%.

[00129] In some embodiments, the glass composition may include SiO_2 in an amount, in mol%, in the range from about 45 to about 80, from about 45 to about 75, from about 45 to about 70, from about 45 to about 65, from about 45 to about 60, from about 45 to about 65, from about 45 to about 65, from about 50 to about 70, from about 55 to about 70, from about 60 to about 70, from about 70 to about 75, from about 70 to about 72, or from about 50 to about 65.

[00130] In some embodiments, the glass composition may include Al_2O_3 in an amount, in mol%, in the range from about 5 to about 28, from about 5 to about 26, from about 5 to about 25, from about 5 to about 24, from about 5 to about 22, from about 5 to about 20, from about 6 to about 30, from about 8 to about 30, from about 10 to about 30, from about 12 to about 30, from about 14 to about 30, from about 16 to about 30, from about 18 to about 30, from about 18 to about 28, or from about 12 to about 15.

[00131] In one or more embodiments, the glass composition may include B_2O_3 in an amount, in mol%, in the range from about 0 to about 8, from about 0 to about 6, from about 0 to about 4, from about 0.1 to about 8, from about 0.1 to about 6, from about 0.1 to about 4, from about 1 to about 10, from about 2 to about 10, from about 4 to about 10, from about 2 to about 8, from about 0.1 to about 5, or from about 1 to about 3. In some instances, the glass composition may be substantially free of B_2O_3. As used herein, the phrase "substantially free" with respect to the components of the glass composition means that the component is not actively or intentionally added to the glass compositions during initial batching or subsequent ion exchange, but may be present as an impurity. For example, a glass may be describe as being substantially free of a component, when the component is present in an amount of less than about 0.1001 mol%.

[00132] In some embodiments, the glass composition may include one or more alkali earth metal oxides, such as MgO, CaO and ZnO. In some embodiments, the total amount of the one or more alkali earth metal oxides may be a non-zero amount up to about 15 mol%. In one or more specific embodiments, the total amount of any of the alkali earth metal oxides may be a non-zero amount up to about 14 mol%, up to about 12 mol%, up to about 10 mol%, up to about 8 mol%, up to about 6 mol%, up to about 4 mol%, up to about 2 mol%, or up about 1.5 mol%. In some embodiments, the total amount, in mol%, of the one or more alkali earth metal oxides may be in the range from about 0.1 to 10, from about 0.1 to 8, from about

0.1 to 6, from about 0.1 to 5, from about 1 to 10, from about 2 to 10, or from about 2.5 to 8. The amount of MgO may be in the range from about 0 mol% to about 5 mol% (e.g., from about 2 mol% to about 4 mol%, from about 0.01 to about 2, or from about 0.001 to about 1). The amount of ZnO may be in the range from about 0 to about 2 mol% (e.g., from about 1 to about 2). The amount of CaO may be from about 0 mol% to about 2 mol%. In one or more embodiments, the glass composition may include MgO and may be substantially free of CaO and ZnO. In one variant, the glass composition may include any one of CaO or ZnO and may be substantially free of the others of MgO, CaO and ZnO. In one or more specific embodiments, the glass composition may include only two of the alkali earth metal oxides of MgO, CaO and ZnO and may be substantially free of the third of the earth metal oxides.

[00133] The total amount, in mol%, of alkali metal oxides R_2O in the glass composition may be in the range from about 5 to about 20, from about 5 to about 18, from about 5 to about 16, from about 5 to about 15, from about 5 to about 14, from about 5 to about 12, from about 5 to about 10, from about 5 to about 8, from about 5 to about 20, from about 6 to about 20, from about 7 to about 20, from about 8 to about 20, from about 9 to about 20, from about 10 to about 20, from about 11 to about 20, from about 12 to about 18, or from about 14 to about 18.

[00134] In one or more embodiments, the glass composition includes Na_2O in an amount in the range from about 0 mol% to about 18 mol%, from about 0 mol% to about 16 mol% or from about 0 mol% to about 14 mol%, from about 0 mol% to about 12 mol%, from about 2 mol% to about 18 mol%, from about 4 mol% to about 18 mol%, from about 6 mol% to about 18 mol%, from about 8 mol% to about 18 mol%, from about 8 mol% to about 14 mol%, from about 8 mol% to about 12 mol%, or from about 10 mol% to about 12 mol%. In some embodiments, the composition may include at least about 4 mol% Na_2O.

[00135] In some embodiments, the amount of Li_2O and Na_2O is controlled to a specific amount or ratio to balance formability and ion exchangeability. For example, as the amount of Li_2O increases, the liquidus viscosity may be reduced, thus preventing some forming methods from being used; however, such glass compositions are ion exchanged to deeper DOC levels, as described herein. The amount of Na_2O can modify liquidus viscosity but can inhibit ion exchange to deeper DOC levels.

[00136] In one or more embodiments, the glass composition may include K_2O in an amount less than about 5 mol%, less than about 4 mol%, less than about 3 mol%, less than about 2 mol%, or less than about 1 mol%. In one or more alternative embodiments, the glass composition may be substantially free, as defined herein, of K_2O.

[00137] In one or more embodiments, the glass composition may include Li_2O in an amount about 0 mol% to about 18 mol%, from about 0 mol% to about 15 mol% or from about 0 mol% to about 10 mol%, from about 0 mol% to about 8 mol%, from about 0 mol% to about 6 mol%, from about 0 mol% to about 4 mol% or from about 0 mol% to about 2 mol%. In some embodiments, the glass composition may include Li_2O in an amount about 2 mol% to about 10 mol%, from about 4 mol% to about 10 mol%, from about 6 mol% to about 10 mol, or from about 5 mol% to about 8 mol%. In one or more alternative embodiments, the glass composition may be substantially free, as defined herein, of Li_2O.

[00138] In one or more embodiments, the glass composition may include Fe_2O_3. In such embodiments, Fe_2O_3 may be present in an amount less than about 1 mol%, less than about 0.9 mol%, less than about 0.8 mol%, less than about 0.7 mol%, less than about 0.6 mol%, less than about 0.5 mol%, less than about 0.4 mol%, less than about 0.3 mol%, less than about 0.2 mol%, less than about 0.1 mol% and all ranges and sub-ranges therebetween. In one or more alternative embodiments, the glass composition may be substantially free, as defined herein, of Fe_2O_3.

[00139] In one or more embodiments, the glass composition may include ZrO_2. In such embodiments, ZrO_2 may be present in an amount less than about 1 mol%, less than about 0.9 mol%, less than about 0.8 mol%, less than about 0.7 mol%, less than about 0.6 mol%, less than about 0.5 mol%, less than about 0.4 mol%, less than about 0.3 mol%, less than about 0.2 mol%, less than about 0.1 mol% and all ranges and sub-ranges therebetween. In one or more alternative embodiments, the glass composition may be substantially free, as defined herein, of ZrO_2.

[00140] In one or more embodiments, the glass composition may include P_2O_5 in a range from about 0 mol% to about 10 mol%, from about 0 mol% to about 8 mol%, from about 0 mol% to about 6mol%, from about 0 mol% to about 4 mol%, from about 0.1 mol% to about 10 mol%, from about 0.1 mol% to about 8 mol%, from about 2 mol% to about 8 mol%, from about 2 mol% to about 6 mol% or from about 2 mol% to about 4 mol%. In some instances, the glass composition may be substantially free of P_2O_5.

[00141] In one or more embodiments, the glass composition may include TiO_2. In such embodiments, TiO_2 may be present in an amount less than about 6 mol%, less than about 4 mol%, less than about 2 mol%, or less than about 1 mol%. In one or more alternative embodiments, the glass composition may be substantially free, as defined herein, of TiO_2. In some embodiments, TiO_2 is present in an amount in the range from about 0.1 mol% to about 6 mol%, or from about 0.1 mol% to about 4 mol%.

[00142] In some embodiments, the glass composition may include various compositional relationships. For example, the glass composition may include a ratio of the amount of Li_2O (in mol%) to the total amount of R_2O (in mol%) in the range from about 0 to about 1, from about 0 to about 0.5, from about 0 to about 0.4, from about 0.1 to about 0.5, or from about 0.2 to about 0.4.

[00143] In some embodiments, the glass composition may include a difference between the total amount of R_2O (in mol%) to the amount of Al_2O_3 (in mol%) (R_2O - Al_2O_3) in the range from about 0 to about 5 (e.g., from about 0 to about 4, from about 0 to about 3, from about 0.1 to about 4, from about 0.1 to about 3, from about 0.1 to about 2 or from about 1 to about 2).

[00144] In some embodiments, the glass composition may include a difference between the total amount of R_xO (in mol%) to the amount of Al_2O_3 (in mol%) (R_xO-Al_2O_3) in the range from about 0 to about 5 (e.g., from about 0 to about 4, from about 0 to about 3, from about 0.1 to about 4, from about 0.1 to about 3, from about 1 to about 3, or from about 2 to about 3).

[00145] In some embodiments, the glass composition may include a ratio of the total amount of R_2O (in mol%) to the amount of Al_2O_3 (in mol%) (R_2O/Al_2O_3) in the range from about 0 to about 5 (e.g., from about 0 to about 4, from about 0 to about 3, from about 1 to about 4, from about 1 to about 3, or from about 1 to about 2).

[00146] In one or more embodiments, the glass composition includes a combined amount of Al_2O_3 and Na_2O greater than about 15 mol% (e.g., greater than 18 mol%, greater than about 20 mol%, or greater than about 23 mol%). The combined amount of Al_2O_3 and Na_2O may be up to and including about 30 mol%, about 32 mol% or about 35 mol%.

[00147] The glass composition of one or more embodiments may exhibit a ratio of the amount of MgO (in mol%) to the total amount of RO (in mol%) in the range from about 0 to about 2.

[00148] In some embodiments, glass composition may be substantially free of nucleating agents. Examples of typical nucleating agents are TiO_2, ZrO_2 and the like. Nucleating agents may be described in terms of function in that nucleating agents are constituents in the glass can initiate the formation of crystallites in the glass.

[00149] In some embodiments, the compositions used for the glass substrate may be batched with 0-2 mol% of at least one fining agent selected from a group that includes Na_2SO_4, NaCl, NaF, NaBr, K_2SO_4, KCl, KF, KBr, and SnO_2. The glass composition according to one or more embodiments may further include SnO_2 in the range from about 0 to about 2, from

about 0 to about 1, from about 0.1 to about 2, from about 0.1 to about 1, or from about 1 to about 2. The glass compositions disclosed herein may be substantially free of As_2O_3 and/or Sb_2O_3.

[00150] In one or more embodiments, the composition may specifically include 62 mol% to 75 mol% SiO_2; 10.5 mol% to about 17 mol% Al_2O_3; 5 mol% to about 13 mol% Li_2O; 0 mol% to about 4 mol% ZnO; 0 mol% to about 8 mol% MgO; 2 mol% to about 5 mol% TiO_2; 0 mol% to about 4 mol% B_2O_3; 0 mol% to about 5 mol% Na_2O; 0 mol% to about 4 mol% K_2O; 0 mol% to about 2 mol% ZrO_2; 0 mol% to about 7 mol% P_2O_5; 0 mol% to about 0.3 mol% Fe_2O_3; 0 mol% to about 2 mol% MnOx; and 0.05 mol% to about0.2 mol% SnO_2.

[00151] In one or more embodiments, the composition may include 67 mol% to about 74 mol% SiO_2; 11 mol% to about 15 mol% Al_2O_3; 5.5 mol% to about 9 mol% Li_2O; 0.5 mol% to about 2 mol% ZnO; 2 mol% to about 4.5 mol% MgO; 3 mol% to about 4.5 mol% TiO_2; 0 mol% to about 2.2 mol% B_2O_3; 0 mol% to about 1 mol% Na_2O; 0 mol% to about 1 mol% K_2O; 0 mol% to about 1 mol% ZrO_2; 0 mol% to about 4 mol% P_2O_5; 0 mol% to about 0.1 mol% Fe_2O_3; 0 mol% to about 1.5 mol% MnOx; and 0.08 mol% to about 0.16 mol%SnO_2.

[00152] In one or more embodiments, the composition may include 70 mol% to 75 mol% SiO_2; 10 mol% to about 15 mol% Al_2O_3; 5 mol% to about 13 mol% Li_2O; 0 mol% to about 4 mol% ZnO; 0.1 mol% to about 8 mol% MgO; 0 mol% to about 5 mol% TiO_2; 0.1 mol% to about 4 mol% B_2O_3; 0.1 mol% to about 5 mol% Na_2O; 0 mol% to about 4 mol% K_2O; 0 mol% to about 2 mol% ZrO_2; 0 mol% to about 7 mol% P_2O_5; 0 mol% to about 0.3 mol% Fe_2O_3; 0 mol% to about 2 mol% MnOx; and 0.05 mol% to about0.2 mol% SnO_2.

[00153] In one or more embodiments, the composition may include 52 mol% to about 65 mol% SiO_2; 14 mol% to about 18 mol% Al_2O_3; 5.5 mol% to about 7 mol% Li_2O; 1 mol% to about 2 mol% ZnO; 0.01 mol% to about 2 mol% MgO; 4 mol% to about 12 mol% Na_2O; 0.1 mol% to about 4 mol% P_2O_5; and 0.01 mol% to about 0.16 mol%SnO_2. In some embodiments, the composition may be substantially free of any one or more of B_2O_3, TiO_2, K_2O and ZrO_2.

[00154] In one or more embodiments, the composition may include at least 0.5 mol% P_2O_5, Na_2O and, optionally, Li_2O, where $Li_2O(mol\%)/Na_2O(mol\%) < 1$. In addition, these compositions may be substantially free of B_2O_3 and K_2O. In some embodiments, the composition may include ZnO, MgO, and SnO_2.

[00155] In some embodiments, the composition may comprise: from about 58 mol% to about 65 mol% SiO_2; from about 11 mol% to about 19 mol% Al_2O_3; from about 0.5 mol% to about 3 mol% P_2O_5; from about 6 mol% to about 18 mol% Na_2O; from 0 mol% to about 6 mol% MgO; and from 0 mol% to about 6 mol% ZnO. In certain embodiments, the composition may comprise from about 63 mol% to about 65 mol% SiO_2; from 11 mol% to about 17 mol% Al_2O_3; from about 1 mol% to about 3 mol% P_2O_5; from about 9 mol% to about 20 mol% Na_2O; from 0 mol% to about 6 mol% MgO; and from 0 mol% to about 6 mol% ZnO.

[00156] In some embodiments, the composition may include the following compositional relationships $R_2O(mol\%)/Al_2O_3(mol\%) < 2$, where $R_2O = Li_2O + Na_2O$. In some embodiments, 65 mol% < $SiO_2(mol\%) + P_2O_5(mol\%)$ < 67 mol%. In certain embodiments, $R_2O(mol\%) + R'O(mol\%) - Al_2O_3(mol\%) + P_2O_5(mol\%) > -3$ mol%, where $R_2O = Li_2O + Na_2O$ and R′O is the total amount of divalent metal oxides present in the composition.

[00157] Other exemplary compositions of glass-based articles prior to being chemically strengthened, as described herein, are shown in Table 1A. Table 1B lists selected physical properties determined for the examples listed in Table 1A. The physical properties listed in Table 1B include: density; low temperature and high temperature CTE; strain, anneal and softening points; 10^{11} Poise, 35 kP, 200 kP, liquidus, and zircon breakdown temperatures; zircon breakdown and liquidus viscosities; Poisson's ratio; Young's modulus; refractive index, and stress optical coefficient. In some embodiments, the glass-based articles and glass substrates described herein have a high temperature CTE of less than or equal to 30 ppm/°C and/or a Young's modulus of at least 70 GPa and, in some embodiments, a Young's modulus of up to 80 GPa.

[00158] Table 1A: Exemplary compositions prior to chemical strengthening.

[00159] Composition (mol%)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
SiO_2	63.77	64.03	63.67	63.91	64.16	63.21	63.50
Al_2O_3	12.44	12.44	11.83	11.94	11.94	11.57	11.73
P_2O_5	2.43	2.29	2.36	2.38	1.92	1.93	1.93
Li_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	16.80	16.81	16.88	16.78	16.80	17.63	16.85
ZnO	0.00	4.37	0.00	4.93	0.00	5.59	5.93
MgO	4.52	0.02	5.21	0.02	5.13	0.02	0.01
SnO_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05
R_2O/Al_2O_3	1.35	1.35	1.43	1.41	1.41	1.52	1.44
Li_2O/Na_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$(R_2O + RO) - Al_2O_3 - P_2O_5$	6.45	6.46	7.89	7.40	8.07	9.74	9.14

Composition (mol%)	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
SiO_2	63.37	63.43	63.56	63.58	63.66	63.62	63.67
Al_2O_3	11.72	12.49	12.63	12.59	12.91	12.85	12.89
P_2O_5	2.00	2.32	2.46	2.46	2.43	2.45	2.47
Li_2O	0.00	0.00	1.42	2.87	0.00	1.42	2.92
Na_2O	16.84	17.16	15.45	14.04	16.89	15.48	13.92
ZnO	6.00	4.54	4.43	4.41	4.04	4.12	4.06
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02
SnO_2	0.05	0.04	0.05	0.05	0.05	0.05	0.05
R_2O/Al_2O_3	1.44	1.37	1.34	1.34	1.31	1.31	1.31
Li_2O/Na_2O	0.00	0.00	0.09	0.20	0.00	0.09	0.21
$(R_2O + RO) - Al_2O_3 - P_2O_5$	9.14	6.90	6.22	6.29	5.62	5.72	5.57

Composition (mol%)	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21
SiO_2	63.55	63.80	63.76	63.88	63.74	64.03	63.68
Al_2O_3	12.92	12.90	12.95	13.48	13.37	13.26	13.19
P_2O_5	2.35	2.34	2.37	2.31	2.34	2.29	2.46
Li_2O	0.00	1.47	2.94	0.00	1.48	2.94	0.00
Na_2O	17.97	16.36	14.85	17.20	15.96	14.37	16.84
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	3.77
MgO	3.17	3.08	3.09	3.08	3.08	3.06	0.02
SnO_2	0.05	0.04	0.05	0.05	0.04	0.04	0.05
R_2O/Al_2O_3	1.39	1.38	1.37	1.28	1.30	1.31	1.28
Li_2O/Na_2O	0.00	0.09	0.20	0.00	0.09	0.20	0.00
$(R_2O + RO) - Al_2O_3 - P_2O_5$	5.87	5.67	5.56	4.48	4.81	4.83	4.98

Composition (mol%)	Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28
SiO_2	63.66	63.76	63.67	63.73	63.73	63.64	63.76
Al_2O_3	14.15	15.31	13.87	14.82	12.93	16.62	16.59
P_2O_5	2.47	2.44	2.47	2.43	2.48	2.47	2.47
Li_2O	1.49	2.98	1.50	2.96	0.00	2.52	4.91
Na_2O	15.31	13.79	15.36	13.93	16.83	14.68	12.20
ZnO	2.85	1.64	0.00	0.00	2.98	0.00	0.00
MgO	0.03	0.03	3.09	2.08	1.00	0.03	0.03
SnO_2	0.05	0.04	0.05	0.05	0.05	0.05	0.05
R_2O/Al_2O_3	1.19	1.10	1.22	1.14	1.30	1.03	1.03
Li_2O/Na_2O	0.10	0.22	0.10	0.21	0.00	0.17	0.40
$(R_2O + RO) - Al_2O_3 - P_2O_5$	3.05	0.70	3.61	1.72	5.40	-1.86	-1.92

Composition (mol%)	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
SiO_2	63.89	63.92	63.77	63.73	63.70	63.65	63.87
Al_2O_3	16.55	15.29	15.27	15.30	15.27	15.22	15.29
P_2O_5	2.47	2.24	2.31	2.39	2.40	2.48	2.37
Li_2O	7.27	3.46	2.98	4.02	4.46	4.96	5.39
Na_2O	9.74	13.46	13.99	12.91	12.51	11.99	11.44
ZnO	0.00	1.56	1.61	1.57	1.58	1.63	1.57
MgO	0.03	0.02	0.02	0.03	0.03	0.02	0.02
SnO_2	0.04	0.04	0.04	0.05	0.04	0.05	0.04
R_2O/Al_2O_3	1.03	1.11	1.11	1.11	1.11	1.11	1.10
Li_2O/Na_2O	0.75	0.26	0.21	0.31	0.36	0.41	0.47
$(R_2O + RO) - Al_2O_3 - P_2O_5$	-1.98	0.97	1.01	0.84	0.90	0.91	0.76

Composition (mol%)	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 42
SiO_2	63.69	63.75	63.70	63.62	63.74	63.77	63.77
Al_2O_3	15.26	15.30	15.27	15.23	15.27	15.27	15.33
P_2O_5	2.45	2.42	2.45	2.46	2.47	2.46	2.44
Li_2O	2.96	2.98	3.94	3.98	4.93	4.93	2.91
Na_2O	13.50	13.46	12.54	12.57	11.49	11.50	13.94
ZnO	2.06	2.01	2.03	2.06	2.03	2.00	0.00
MgO	0.02	0.03	0.02	0.03	0.03	0.03	1.57
SnO_2	0.05	0.04	0.04	0.05	0.04	0.05	0.04
R_2O/Al_2O_3	1.08	1.08	1.08	1.09	1.08	1.08	1.10
Li_2O/Na_2O	0.22	0.22	0.31	0.32	0.43	0.43	0.21
$(R_2O + RO) - Al_2O_3 - P_2O_5$	0.83	0.77	0.80	0.95	0.73	0.73	0.66

Composition (mol%)	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49
SiO_2	63.69	63.81	63.65	63.71	63.62	63.65	63.62
Al_2O_3	15.25	15.26	15.33	15.32	15.24	15.68	15.67
P_2O_5	2.43	2.41	2.46	2.44	2.47	2.44	2.48

Composition (mol%)	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49
Li_2O	4.00	4.89	2.96	4.01	4.91	6.07	6.06
Na_2O	13.01	12.03	13.29	12.25	11.42	10.93	10.53
ZnO	0.00	0.00	2.24	2.20	2.27	1.17	1.57
MgO	1.57	1.56	0.03	0.03	0.02	0.02	0.02
SnO_2	0.05	0.04	0.05	0.04	0.05	0.04	0.05
R_2O/Al_2O_3	1.12	1.11	1.06	1.06	1.07	1.08	1.06
Li_2O/Na_2O	0.31	0.41	0.22	0.33	0.43	0.56	0.58
$(R_2O + RO) - Al_2O_3 - P_2O_5$	0.90	0.81	0.73	0.73	0.91	0.08	0.04

Composition (mol%)	Ex. 50	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56
SiO_2	63.60	63.89	63.84	63.90	63.88	64.74	60.17
Al_2O_3	15.65	16.09	16.47	16.87	16.97	15.25	18.58
P_2O_5	2.46	2.42	2.43	2.43	2.42	0.98	1.90
Li_2O	6.13	6.80	7.84	8.75	9.78	5.28	5.16
Na_2O	10.29	9.97	8.96	7.99	6.88	12.09	12.58
ZnO	1.81	0.78	0.39	0.00	0.00	1.61	1.55
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02
SnO_2	0.04	0.04	0.04	0.04	0.04	0.03	0.03
R_2O/Al_2O_3	1.05	1.04	1.02	0.99	0.98	1.14	0.96
Li_2O/Na_2O	0.60	0.68	0.87	1.10	1.42	0.44	0.41
$(R_2O + RO) - Al_2O_3 - P_2O_5$	0.14	-0.94	-1.68	-2.54	-2.70	2.78	-1.16

Composition (mol%)	Ex. 57	Ex. 58	Ex. 59	Ex. 60	Ex. 61	Ex. 62	Ex. 63	Ex. 64
SiO_2	58.32	63.3	63.3	63.3	63.3	63.3	63.3	63.46
Al_2O_3	18.95	15.25	15.65	16.2	15.1	15.425	15.7	15.71
P_2O_5	2.42	2.5	2.5	2.5	2.5	2.5	2.5	2.45
Li_2O	4.96	6	7	7.5	6	7	7.5	6.37
Na_2O	13.74	10.7	9.7	9.45	10.55	9.475	8.95	10.69
ZnO	1.56	1.2	0.8	0	2.5	2.25	2	1.15
MgO	0.02	1	1	1	0	0	0	0.06
SnO_2	0.03	0.05	0.05	0.05	0.05	0.05	0.05	0.04
R_2O/Al_2O_3	0.99	1.10	1.07	1.05	1.10	1.07	1.05	1.09
Li_2O/Na_2O	0.36	0.56	0.72	0.79	0.57	0.74	0.84	0.6
$(R_2O + RO) - Al_2O_3 - P_2O_5$	-1.09	1.15	0.35	-0.75	1.45	0.80	0.25	-1.1

Table 2. Selected physical properties of the glasses listed in Table 1.

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Density (g/cm^3)	2.434	2.493	2.434	2.504	2.44	2.514	2.519

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Low temperature CTE 25-300 °C (ppm/°C)	8.9	8.62	8.95	8.6	8.82	8.71	8.54
High temperature CTE (ppm/°C)	17.67	19.1	17.16	21	18.12	20	20.11
Strain pt. (°C)	630	591	612	580	605	580	589
Anneal pt. (°C)	683	641	662	628	651	629	639
10^{11} Poise temperature (°C)	770	725	748	710	734	711	721
Softening pt. (°C)	937	888	919	873	909	868	874
$T^{35\ kP}$ (°C)				1167	1180	1158	1160
$T^{200\ kP}$ (°C)				1070	1083	1061	1064
Zircon breakdown temperature (°C)		1205		1220	1170	1185	1205
Zircon breakdown viscosity (P)				1.56 x10^4	4.15 x10^4	2.29 x10^4	1.74 x10^4
Liquidus temperature (°C)		980		990	975	990	1000
Liquidus viscosity (P)				1.15 x10^6	2.17 x10^6	9.39 x10^5	7.92 x10^5
Poisson's ratio	0.200	0.211	0.206	0.214	0.204	0.209	0.211
Young's modulus (GPa)	69.2	68.8	69.4	68.5	69.6	68.3	69.0
Refractive index at 589.3 nm	1.4976	1.5025	1.4981	1.5029	1.4992	1.5052	1.506
Stress optical coefficient (nm/mm/MPa)	2.963	3.158	3.013	3.198	2.97	3.185	3.234

	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Density (g/cm^3)	2.516	2.501	2.498	2.493	2.493	2.492	2.486
Low temperature CTE 25-300 °C (ppm/°C)	8.35	8.67	8.87	8.49	8.65	8.71	8.49
High temperature CTE (ppm/°C)	20.11	20.6	20.94		19.52	20.77	
Strain pt. (°C)	590	589	591	584	600	579	588
Anneal pt. (°C)	641	639	640	628	652	620	630
10^{11} Poise temperature (°C)	726	724	720	704	738	695	704

	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Softening pt. (^oC)	888	890	865	857	900	867	860
$T^{35\ kP}$ (^oC)	1170	1176	1159	1139	1197	1169	
$T^{200\ kP}$ (^oC)	1073	1080	1061	1041	1099	1070	
Zircon breakdown temperature (^oC)	1195	1195	1210	1225	1195	1195	1220
Zircon breakdown viscosity (P)	2.33 $x10^4$	2.58 $x10^4$	1.60 $x10^4$	9.94 $x10^3$	3.63 $x10^4$	2.35 $x10^4$	
Liquidus temperature (^oC)	1005	990	990	980	990	980	980
Liquidus viscosity (P)	8.69 $x10^4$	1.48E+06	9.02E+05	7.10E+05	2.19E+06	1.33E+06	
Poisson's ratio	0.211	0.205	0.208	0.209	0.209	0.210	0.217
Young's modulus (GPa)	69.0	68.7	71.4	73.5	68.4	71.6	74.0
Refractive index at 589.3 nm	1.506	1.5036	1.505	1.5063	1.5026	1.5041	1.5052
Stress optical coefficient (nm/mm/MPa)	3.234	3.194	3.157	3.131	3.18	3.156	3.131

	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21
Density (g/cm^3)	2.433	2.429	2.426	2.431	2.428	2.433	2.486
Low temperature CTE 25-300 ^oC (ppm/^oC)	9.15	9.16	8.83	8.97	8.97	8.79	8.45
High temperature CTE (ppm/^oC)	20	20	21	17.3	20		
Strain pt. (^oC)	615	606	599	633	616	611	602
Anneal pt. (^oC)	662	659	653	684	670	665	653
10^{11} Poise temperature (^oC)	747	745	741	771	758	751	739
Softening pt. (^oC)	935	903	901	943	918	905	910
$T^{35\ kP}$ (^oC)	1182	1166	1152	1221	1185	1167	1207
$T^{200\ kP}$ (^oC)	1083	1066	1051	1122	1084	1066	1108
Zircon breakdown temperature (^oC)							
Zircon breakdown viscosity (P)							
Liquidus temperature							

	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21
(°C)							
Liquidus viscosity (P)							
Poisson's ratio	0.203	0.207	0.205	0.209	0.199		0.207
Young's modulus (GPa)	68.9	71.2	72.7	69.4	70.9		68.1
Refractive index at 589.3 nm	1.4964	1.4981	1.4991	1.4965	1.4984	1.5006	1.5019
Stress optical coefficient (nm/mm/MPa)	2.994	3.022	2.982	2.979	2.99	0	3.173

	Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28
Density (g/cm^3)	2.468	2.448	2.434	2.428	2.47	2.419	2.414
Low temperature CTE 25-300 °C (ppm/°C)	8.6	8.23	8.91	8.25	8.66	8.52	8.17
High temperature CTE (ppm/°C)	19.52		19.49				19.47
Strain pt. (°C)	596	595	638	616	608	640	620
Anneal pt. (°C)	644	649	695	656	654	700	677
10^{11} Poise temperature (°C)	728	741	785	732	736	798	771
Softening pt. (°C)	905	922	941	925	911	978	946
$T^{35 kP}$ (°C)	1217	1227	1209	1215	1209	1283	1249
$T^{200 kP}$ (°C)	1115	1125	1109	1115	1107	1184	1150
Zircon breakdown temperature (°C)	1185	1185	1180	1185			1185
Zircon breakdown viscosity (P)	5.86E+04	6.91E+04	5.59E+04	5.72E+04			1.05E+05
Liquidus temperature (°C)	975	980	1080	1025			940
Liquidus viscosity (P)	4.14E+06	4.52E+06	3.56E+05	1.27E+06			2.92E+07
Poisson's ratio	0.210		0.204	0.210	0.212		0.213
Young's modulus (GPa)	71.4		71.6	73.5	68.8		76.9
Refractive index at 589.3 nm	1.502	1.5025	1.4996	1.5008	1.5006	1.4987	1.5014
Stress optical coefficient (nm/mm/MPa)	3.123	3.03	3.001	3.021	3.148	3.039	3.015

	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
Density (g/cm^3)	2.408	2.446	2.448	2.446	2.445	2.443	2.442
Low temperature CTE 25-300 °C (ppm/°C)	7.86	8.29	8.38	8.17	8.14	8.04	7.97
High temperature CTE (ppm/°C)	18.57					19.71	
Strain pt. (°C)	610	591	595	585	580	574	577
Anneal pt. (°C)	665	645	649	638	633	627	629
10^{11} Poise temperature (°C)	755	736	740	726	722	717	717
Softening pt. (°C)	924	915	919	894	894	895	890
$T^{35\ kP}$ (°C)	1216	1223	1227	1216	1210	1203	1196
$T^{200\ kP}$ (°C)	1120	1122	1126	1114	1108	1102	1095
Zircon breakdown temperature (°C)	1210	1175	1180	1190	1195	1210	1205
Zircon breakdown viscosity (P)	3.86E+04	7.72E+04	7.55E+04	5.29E+04	4.43E+04	3.14E+04	3.04E+04
Liquidus temperature (°C)	1080	990	975	975	975	975	980
Liquidus viscosity (P)	4.55E+05	3.28E+06	5.43E+06	3.80E+06	3.33E+06	3.02E+06	2.29E+06
Poisson's ratio	0.211	0.206	0.202	0.21	0.204	0.204	0.203
Young's modulus (GPa)	75.0	73.91	73.02	74.60	74.67	75.15	75.43
Refractive index at 589.3 nm	1.5053	1.503	1.5025	1.5035	1.5041	1.5046	1.5053
Stress optical coefficient (nm/mm/MPa)	3.002	3.074	3.083	3.071	3.059	3.016	3.053

	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
Density (g/cm^3)	2.408	2.446	2.448	2.446	2.445	2.443	2.442
Low temperature CTE 25-300 °C (ppm/°C)	7.86	8.29	8.38	8.17	8.14	8.04	7.97

	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
High temperature CTE (ppm/^oC)	18.57					19.71	
Strain pt. (^oC)	610	591	595	585	580	574	577
Anneal pt. (^oC)	665	645	649	638	633	627	629
10^{11} Poise temperature (^oC)	755	736	740	726	722	717	717
Softening pt. (^oC)	924	915	919	894	894	895	890
$T^{35\ kP}$ (^oC)	1216	1223	1227	1216	1210	1203	1196
$T^{200\ kP}$ (^oC)	1120	1122	1126	1114	1108	1102	1095
Zircon breakdown temperature (^oC)	1210	1175	1180	1190	1195	1210	1205
Zircon breakdown viscosity (P)	3.86E+04	7.72E+04	7.55E+04	5.29E+04	4.43E+04	3.14E+04	3.04E+04
Liquidus temperature (^oC)	1080	990	975	975	975	975	980
Liquidus viscosity (P)	4.55E+05	3.28E+06	5.43E+06	3.80E+06	3.33E+06	3.02E+06	2.29E+06
Poisson's ratio	0.211	0.206	0.202	0.21	0.204	0.204	0.203
Young's modulus (GPa)	75.0	73.91	73.02	74.60	74.67	75.15	75.43
Refractive index at 589.3 nm	1.5053	1.503	1.5025	1.5035	1.5041	1.5046	1.5053
Stress optical coefficient (nm/mm/MPa)	3.002	3.074	3.083	3.071	3.059	3.016	3.053

	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 42
Density (g/cm^3)	2.453	2.453	2.452	2.451	2.449	2.449	2.425
Low temperature CTE 25-300 ^oC (ppm/^oC)	8.17	8.14	7.97	8.01	7.79	7.9	8.54
High temperature CTE (ppm/^oC)					20.56		
Strain pt. (^oC)	595	595	584	587	578	584	617
Anneal pt. (^oC)	649	649	638	640	630	637	663
10^{11} Poise temperature (^oC)	740	741	729	730	718	726	746
Softening pt. (^oC)	918	921	905	907	894	901	929
$T^{35\ kP}$ (^oC)	1229	1232	1212	1219	1200	1204	1232
$T^{200\ kP}$ (^oC)	1128	1131	1111	1118	1100	1103	1132

	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 42
Zircon breakdown temperature (°C)	1185		1200		1210		
Zircon breakdown viscosity (P)	7.20E+04		4.26E+04		3.00E+04		
Liquidus temperature (°C)	995		990		965		
Liquidus viscosity (P)	3.33E+06		2.51E+06		3.71E+06		
Poisson's ratio	0.208		0.206		0.206		
Young's modulus (GPa)	73.70		74.67		75.50		
Refractive index at 589.3 nm	1.5032		1.5042		1.5054		1.5005
Stress optical coefficient (nm/mm/MPa)	3.093		3.071		3.072		3.033

	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49	Ex. 50
Density (g/cm^3)	2.424	2.422	2.455	2.454	2.454	2.434	2.439	2.443
Low temperature coefficient of thermal expansion 25 - 300 °C (ppm/°C)	8.48	8.34	8.03	7.88	7.76	7.87	7.71	7.63
High temperature coefficient of thermal expansion (ppm/°C)								
Strain pt. temperature (°C)	614	594	595	586	579	580	581	579
Anneal pt. temperature (°C)	659	640	649	639	630	633	633	632
10^{11} Poise temperature (°C)	739	722	740	729	718	722	721	721
Softening pt. temperature (°C)	912	899	918	909	898	892	893	895
35 kP temperature (°C)	1216	1204		1212	1200	1203	1203	1203
200 kP temperature (°C)	1116	1102		1113	1099	1105	1102	1103

	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49	Ex. 50
Zircon breakdown temperature (°C)								
Zircon breakdown viscosity (P)								
Liquidus temperature (°C)			985		965	1005	1010	1030
Liquidus viscosity (P)					4.E+06	1.78E+06	1.34E+06	8.98E+05
Poisson's ratio						0.211	0.21	0.213
Young's modulus (GPa)						76.32	76.60	76.81
Refractive index at 589.3 nm	1.5014	1.5026	1.5036	1.5047	1.5061	1.505	1.5059	1.5064
Stress optical coefficient (nm/mm/MPa)	2.965	2.981	3.082	3.057	3.063	3.025	3.004	3.046

	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57
Density (g/cm^3)	2.424	2.431	2.403	2.4	2.45	2.462	2.468
Low temperature CTE 25-300 °C (ppm/°C)	77.1	76.1	74.3	73.1	80.2	79.7	83.6
High temperature CTE (ppm/°C)							
Strain pt. (°C)	588	599	611	612	580	611	597
Anneal pt. (°C)	640	651	665	665	631	663	649
10^{11} Poise temperature (°C)	728	738	753	752	718	750	735
Softening pt. (°C)	900.4	907.5	916	912.5	892.2	915.6	899.4
$T^{35\ kP}$ (°C)	1204	1209	1209	1202	1206	1205	1184
$T^{200\ kP}$ (°C)	1106	1113	1113	1106	1102	1111	1093
Zircon breakdown temperature (°C)							
Zircon breakdown viscosity (P)							
Liquidus temperature (°C)	1060	1115	1160	1205			
Liquidus viscosity (P)	5.11E+05	1.90E+05	8.18E+04	3.32E+04			
Poisson's ratio	0.211	0.212	0.208	0.214			

	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57
Young's modulus (GPa)	77.01	78.05	77.57	78.74			
Refractive index at 589.3 nm	1.5054	1.5055	1.5059	1.5072			
Stress optical coefficient (nm/mm/MPa)	3.011	2.98	2.982	2.964			

	Ex. 64
Density (g/cm^3)	2.428
CTE 25-300 °C (ppm/°C)	7.8
Strain pt. (°C)	571
Anneal pt. (°C)	622
10^{11} Poise temperature (°C)	
Softening pt. (°C)	881.4
$T^{35 kP}$ (°C)	
$T^{200 kP}$ (°C)	1645
Zircon breakdown temperature (°C)	
Zircon breakdown viscosity (P)	
Liquidus temperature (°C)	1000
Liquidus viscosity (P)	1524280
Poisson's ratio	0.211
Young's modulus (GPa)	76.3
Refractive index at 589.3 nm	1.51
Stress optical coefficient (nm/mm/MPa)	3.02

[00160] Where the glass-based article includes a glass-ceramic, the crystal phases may include β-spodumene, rutile, gahnite or other known crystal phases and combinations thereof.

[00161] The glass-based article may be substantially planar, although other embodiments may utilize a curved or otherwise shaped or sculpted substrate. In some instances, the glass-based article may have a 3D or 2.5D shape. The glass-based article may be substantially optically clear, transparent and free from light scattering. The glass-based article may have a refractive index in the range from about 1.45 to about 1.55. As used herein, the refractive index values are with respect to a wavelength of 550 nm.

[00162] Additionally or alternatively, the thickness of the glass-based article may be constant along one or more dimension or may vary along one or more of its dimensions for aesthetic and/or functional reasons. For example, the edges of the glass-based article may be thicker as compared to more central regions of the glass-based article. The length, width and thickness dimensions of the glass-based article may also vary according to the article application or use.

[00163] The glass-based article may be characterized by the manner in which it is formed. For instance, where the glass-based article may be characterized as float-formable (i.e., formed by a float process), down-drawable and, in particular, fusion-formable or slot-drawable (i.e., formed by a down draw process such as a fusion draw process or a slot draw process).

[00164] A float-formable glass-based article may be characterized by smooth surfaces and uniform thickness is made by floating molten glass on a bed of molten metal, typically tin. In an example process, molten glass that is fed onto the surface of the molten tin bed forms a floating glass ribbon. As the glass ribbon flows along the tin bath, the temperature is gradually decreased until the glass ribbon solidifies into a solid glass-based article that can be lifted from the tin onto rollers. Once off the bath, the glass glass-based article can be cooled further and annealed to reduce internal stress. Where the glass-based article is a glass ceramic, the glass-based article formed from the float process may be subjected to a ceramming process by which one or more crystalline phases are generated.

[00165] Down-draw processes produce glass-based articles having a uniform thickness that possess relatively pristine surfaces. Because the average flexural strength of the glass-based article is controlled by the amount and size of surface flaws, a pristine surface that has had minimal contact has a higher initial strength. When this high strength glass-based article is then further strengthened (e.g., chemically), the resultant strength can be higher than that of a glass-based article with a surface that has been lapped and polished. Down-drawn glass-based articles may be drawn to a thickness of less than about 2 mm. In addition, down drawn glass-based articles have a very flat, smooth surface that can be used in its final application

without costly grinding and polishing. Where the glass-based article is a glass ceramic, the glass-based article formed from the down draw process may be subjected to a ceramming process by which one or more crystalline phases are generated.

[00166] The fusion draw process, for example, uses a drawing tank that has a channel for accepting molten glass raw material. The channel has weirs that are open at the top along the length of the channel on both sides of the channel. When the channel fills with molten material, the molten glass overflows the weirs. Due to gravity, the molten glass flows down the outside surfaces of the drawing tank as two flowing glass films. These outside surfaces of the drawing tank extend down and inwardly so that they join at an edge below the drawing tank. The two flowing glass films join at this edge to fuse and form a single flowing glass-based article. The fusion draw method offers the advantage that, because the two glass films flowing over the channel fuse together, neither of the outside surfaces of the resulting glass-based article comes in contact with any part of the apparatus. Thus, the surface properties of the fusion drawn glass-based article are not affected by such contact. Where the glass-based article is a glass ceramic, the glass-based article formed from the fusion process may be subjected to a ceramming process by which one or more crystalline phases are generated.

[00167] The slot draw process is distinct from the fusion draw method. In slow draw processes, the molten raw material glass is provided to a drawing tank. The bottom of the drawing tank has an open slot with a nozzle that extends the length of the slot. The molten glass flows through the slot/nozzle and is drawn downward as a continuous glass-based article and into an annealing region.

[00168] The glass-based article may be acid polished or otherwise treated to remove or reduce the effect of surface flaws.

[00169] Another aspect of this disclosure pertains to a method of forming a fracture-resistant glass-based article. The method includes providing a glass-based substrate having a first surface and a second surface defining a thickness of about 1 millimeter or less and generating a stress profile in the glass-based substrate, as described herein to provide the fracture-resistant glass-based article. In one or more embodiments, generating the stress profile comprises ion exchanging a plurality of alkali ions into the glass-based substrate to form a non-zero alkali metal oxide concentration that varies along a substantial portion of the thickness (as described herein) or along the entire thickness. In one example, generating the stress profile includes immersing the glass-based substrate in a molten salt bath including nitrates of $Na+$, $K+$, $Rb+$, $Cs+$ or a combination thereof, having a temperature of about 350 °C or greater (e.g., about 350 °C to about 500 °C). In one example, the molten bath may

include $NaNO_3$, KNO_3 or a combination thereof, and may have a temperature of about 485 °C or less. In another example, the bath may include a mixture of $NaNO_3$ and KNO_3 and have a temperature of about 460 °C. The glass-based substrate may be immersed in the bath for about 2 hours or more, up to about 48 hours (e.g., from about 2 hours to about 10 hours, from about 2 hours to about 8 hours, from about 2 hours to about 6 hours, from about 3 hours to about 10 hours, or from about 3.5 hours to about 10 hours).

[00170] In some embodiments, the method may include chemically strengthening or ion exchanging the glass-based substrate in a single bath or in more than one step using successive immersion steps in more than one bath. For example, two or more baths may be used successively. The composition of the one or more baths may include a single metal (e.g., Ag+, Na+, K+, Rb+, or Cs+) or a combination of metals in the same bath. When more than one bath is utilized, the baths may have the same or different composition and/or temperature as one another. The immersion times in each such bath may be the same or may vary to provide the desired stress profile.

[00171] In one or more embodiments of the method, a second bath or subsequent baths may be utilized to generate a greater surface CS. In some instances, the method includes immersing the glass-based substrate in the second or subsequent baths to generate a greater surface CS, without significantly influencing the chemical depth of layer and/or the DOC. In such embodiments, the second or subsequent bath may include a single metal (e.g., KNO_3 or $NaNO_3$) or a mixture of metals (KNO_3 and $NaNO_3$). The temperature of the second or subsequent bath may be tailored to generate the greater surface CS. In some embodiments, the immersion time of the glass-based substrate in the second or subsequent bath may also be tailored to generate a greater surface CS without influencing the chemical depth of layer and/or the DOC. For example, the immersion time in the second or subsequent baths may be less than 10 hours (e.g., about 8 hours or less, about 5 hours or less, about 4 hours or less, about 2 hours or less, about 1 hour or less, about 30 minutes or less, about 15 minutes or less, or about 10 minutes or less).

[00172] In one or more alternative embodiments, the method may include one or more heat treatment steps which may be used in combination with the ion-exchanging processes described herein. The heat treatment includes heat treating the glass-based article to obtain a desired stress profile. In some embodiments, heat treating includes annealing, tempering or heating the glass-based substrate to a temperature in the range from about 300°C to about 600°C. The heat treatment may last for 1 minute up to about 18 hours. In some

embodiments, the heat treatment may be used after one or more ion-exchanging processes, or between ion-exchanging processes.

Examples

[00173] Various embodiments will be further clarified by the following examples. In the Examples, prior to being strengthened, the Examples are referred to as "substrates". After being subjected to strengthening, the Examples are referred to as "articles" or "glass-based articles".

EXAMPLE 1

[00174] Examples 1A-1G included glass substrates having a nominal composition of about 63.46 mol% SiO_2, 15.71 mol% Al_2O_3, 6.37 mol% Li_2O, 10.69 mol% Na_2O, 0.06 mol% MgO, 1.15 mol% ZnO, 2.45 mol% P_2O_5, and 0.04 mol% SnO_2. The glass substrates have a thickness of 0.8 mm. The glass substrates of Examples 1A-1G were ion exchanged in a molten salt bath including 100% $NaNO_3$ and having a temperature of about 390 °C, according to the conditions provided in Table 2. The resulting glass-based articles exhibited maximum CT values, which are plotted as a function of ion exchange time in Figure 5.

[00175] Table 2: Ion exchange conditions for Examples 1A-1G.

Example	Time immersed in bath (hours)	Maximum CT
1A	0.5	30
1B	1	42
1C	1.5	52
1D	2	56
1E	3.75	67
1F	8	63
1G	16	55

[00176] The stress profile for Example 1E was measured using a refracted near-field (RNF) measurement, as described in U.S. Patent No. 8,854,623, entitled "Systems and methods for measuring a profile characteristic of a glass sample", which is incorporated herein by reference in its entirety. Figure 6 shows the measured stress as a function of depth extending from the surface of the glass-based article of Example 1E into the glass-based article. The stress at specific depths is shown in Table 3, including at the "knee" which is the depth at which the slope of the stress changes drastically.

[00177] Table 3: Stress at specific depths of Example 1E.

Depth (micrometers)	Stress (MPa)
12 (“knee”)	161
50	95
100	36
150	0

EXAMPLE 2

[00178] Example 2A included a glass substrate having the same composition as Example 1 and a thickness of 0.8 mm. The glass substrate was ion exchanged in a single molten salt bath including 51% KNO3 and 49% $NaNO_3$, and having a temperature of about 380° C, for 3.75 hours. The resulting glass-based article exhibited the stress profile as described in Table 4.

[00179] Table 4: Stress profile of Example 2A.

Surface Compressive Stress	500 MPa
Depth of layer for potassium	12 micrometers
Stress at DOL of potassium	161 MPa
Maximum CT	70 MPa
DOC	150 micrometers

[00180] Glass-based articles according to Example 2A were subjected to AROR testing as described herein. One set of glass-based articles was abraded using a load or pressure of 5 psi, a second set of glass-based articles was abraded using a load or pressure of 25 psi, and a third set of glass-based articles was abraded using a load or pressure of 45 psi. The AROR data is shown in Figure 7. As shown in Figure 7, all of the glass-based articles according to Example 2A exhibited an average load to failure of greater than about 20 kgf.

[00181] Glass-based articles according to Example 2A were retrofitted onto identical mobile phone devices. The phone devices were dropped from incremental heights starting at 20 centimeters onto 180 grit sandpaper. If a glass-based article survived the drop from one height (e.g., 20 cm), the mobile phone was dropped again from a greater height (e.g., 30 cm, 40 cm, 50 cm, etc.) up to a height of 225 cm. The surviving glass-based articles were then dropped onto 30 grit sandpaper (in the same phone devices). The height at which the glass-

based article failed on both 180 grit sandpaper and 30 grit sandpaper is plotted in Figure 8. As shown in Figure 8, all but two glass-based articles of Example 2A survived being dropped onto 180 grit sandpaper up to heights of about 225 cm (providing an average survival drop height of about 216 cm). The average survival drop height onto 30 grit sandpaper was 66 cm, with some surviving over 100 cm drop heights.

[00182] The glass based articles according to Example 2A exhibited a dielectric constant of about 6.9 to about 7.05 over a frequency range from about 480 mHz to about 3000 mHz. The glass-based articles according to Example 2A exhibited a dielectric loss tangent in the range from about 0.012 to about 0.015 over a frequency range from about 480 mHz to about 3000 mHz.

[00183] The refractive index of the glass-based articles according to Example 2A is in the range from about 1.158 to about 1.49 over a range from about 380 nm to about 1550 nm, and from about 1.518 to about 1.497 over a wavelength range from about 380 nm to about 800 nm.

[00184] The glass-based articles according to Example 2A were subjected to various chemical treatments as shown in Table 5. The chemical durability of the glass-based articles was compared to Comparative Examples 2E, 2F and 2G. Comparative Example 2E was a glass substrate having a nominal composition of 64.3 mol% SiO_2, 7.02 mol% B_2O_3, 14 mol% Al_2O_3, 14 mol% Na_2O, 0.5 mol% K_2O, 0.03 mol% Fe_2O_3, and 0,1 mol% SnO_2. Comparative Example 2F was a glass substrate having a nominal composition of 64.75 mol% SiO_2, 5 mol% B_2O_3, 14 mol% Al_2O_3, 13.75 mol% Na_2O, 2.4 mol% MgO, and 0.08 mol% SnO_2. Comparative Example 2G included a glass substrate having a nominal composition of 57.5 mol% SiO_2, 16.5 mol% Al_2O_3, 16.71 mol% Na_2O, 2.8 mol% MgO and 0.05 mol% SnO_2.

[00185] Table 5: Chemical durability of Example 2A.

Chemical Treatment	Weight loss (mg/cm2)			
	Comparative Example 2E	Comparative Example 2F	Comparative Example 2G	Example 2A
5% w/w HCl, 95 °C, 24 hours	29.3	6.7	50	5.77
5% w/w NaOH, 95 °C, 6 hours	2.8	2.4	5.8	2.68
10% HF, room temperature,	20.8	18.1	37.4	24.03

20 minutes				
10% ammonium bifluoride (ABF), room temperature, 20 minutes	2	2.7	3.2	0.98

EXAMPLE 3

[00186] Example 3A included glass substrates having the same composition as Example 1 and a thickness of 0.8mm. Comparative Example 3B included glass substrates having the same composition as Comparative Example 2G and a thickness of 0.8 mm. The glass substrates of Example 3A were chemically strengthened in a single step using a single bath, as described in Table 6. The glass substrates of Comparative Example 3B was ion exchanged in a two-step process, as described in Table 6.

[00187] Table 6: Ion exchange conditions for Example 3A and Comparative Example 3B.

		Example 3A	Comparative Example 3B
1st Step	Molten salt bath composition	49% NaNO3/51% KNO3	49% NaNO3/51% KNO3
	Bath Temperature	380 °C	460 °C
	Immersion time	3.75 hours	14 hours
2nd Step	Molten salt bath composition	-	99.5% KNO3/0.5% NaNO3
	Bath Temperature	-	390 °C
	Immersion time	-	0.25 hours
Properties of resulting glass article	Surface CS	500 MPa	825 MPa
	DOL of potassium	12 micrometers	10 micrometers
	Stress at DOL of potassium	160 MPa	220 MPa
	DOC	150 micrometers	100 micrometers

[00188] The glass-based articles according to Example 3A and Comparative Example 3B were retrofitted onto identical mobile phone devices. The phone devices were dropped from incremental heights starting at 20 centimeters onto 30 grit sandpaper. The height at which the glass-based article failed on 30 grit sandpaper is plotted in Figure 9. As shown in Figure 9,

the glass-based articles of Example 3A exhibited an average survival drop height that is more than two times (i.e., 91 cm) the average survival drop height of Comparative Example 3B (i.e., 38 cm).

[00189] Glass-based articles according to Example 3A and Comparative Example 3B were subjected to AROR testing, as described herein, using a load or pressure of 25 psi. The glass-based substrates of Example 3A exhibited an average load to failure of about 30 kgf, while the glass-based substrates of Comparative Example 3B exhibited an average load to failure of about 27 kgf, as shown in Figure 10. When the abrasion load or pressure was increased to 45 psi, the difference in average load to failure for Example 3A and Comparative Example 3B increased. Specifically, under a 45 psi load or pressure, Example 3A exhibited an average load to failure of about 25.9 kgf, while Comparative Example 3B exhibited an average load to failure of about 19.6 kgf, as shown in Figure 11.

EXAMPLE 4

[00190] Glass substrates having a nominal composition of 57.5 mol% SiO_2, 16.5 mol% Al_2O_3, 16.7 mol% Na_2O, 2.5 mol% MgO, and 6.5 mol% P_2O_5, and having a thicknesses of about 0.4 mm, 0.55 mm, or 1 mm were subjected to chemical strengthening. The thicknesses and conditions of chemical strengthening are shown in Table 7.

[00191] Table 7: Thickness and chemical strengthening conditions for Examples 4A-4D.

Ex.	Thickness	Bath Composition	Bath Temperature
6A	0.4 mm	80% KNO3, 20% NaNO3	430 °C
6B	0.55 mm	80% KNO_3, 20% $NaNO_3$	430 °C
6C	0.55 mm	90% KNO_3, 10% $NaNO_3$	430 °C
6D	1.0 mm	70% KNO_3, 30% $NaNO_3$	430 °C

[00192] Example 4A was immersed in a molten salt bath, as indicted in Table 7, for 4 hours, 8 hours, 16 hours, 32 hours, 64 hours and 128 hours (Examples 4A-1 through 4A-6). Example 4B was immersed in a molten salt bath, as indicated in Table 7, for 4 hours, 8 hours, 16 hours, 32 hours, 64 hours and 128 hours (Examples 4B-1 through 4B-6). Example 4C was immersed in a molten salt bath, as indicated in Table 7, for 1 hour, 2 hours, 4 hours, 8 hours,

16 hours and 32 hours (Examples 4C-1 through 4C-6). Example 4D was immersed in a molten salt bath, as indicated in Table 7, for 4 hours, 8 hours, 16 hours, 32 hours, 64 hours and 128 hours (Examples 4D-1 through 4D-6). The stress profiles of Examples 4A-1 through 4A-6, 4B-1 through 4B-6, 6C-1 through 4C-6, and 4D-1 through 4D-6 are shown in Figures 12, 14, 16 and 18, respectively. In Figures 12, 14, 16 and 18, the depth or thickness of the glass articles is plotted on the x-axis and stress is plotted on the y-axis. The positive stress values are CT values and the negative stress values are the CS values.

[00193] The CT and DOC values as a function of time immersed in the molten salt bath for Examples 4A-1 through 4A-6, Examples 4B-1 through 4B-6, Examples 4C-1 through 4C-6 and 4D-1 through 4D-6, are shown in Figures 13, 15, 17, and 19, respectively.

EXAMPLE 5

[00194] Glass substrates having a nominal composition as shown in Table 8 and having a thicknesses of about 0.8 mm each were subjected to chemical strengthening in a molten salt bath including a mixture of $NaNO_3$ and $NaSO_4$ and a temperature of 500 °C for 15 minutes (Comparative Example 8A) and for 16 hours (Example 8B).

[00195] Table 8: Composition of the glass substrate of Example 5, prior to chemical strengthening.

Example ⇒▶ / **Oxide [mole%]**	**1**
SiO_2	69.2
Al_2O_3	12.6
B_2O_3	1.8
Li_2O	7.7
Na_2O	0.4
MgO	2.9
ZnO	1.7
TiO_2	3.5
SnO_2	0.1
$\frac{[Li_2O+Na_2O+MgO+ZnO+K_2O]}{[Al_2O_3+B_2O_3]}$	$\frac{12.7}{14.4} = 0.88$
$\frac{[TiO_2+SnO_2]}{[SiO_2+B_2O_3]}$	$\frac{3.6}{71} =0.051$

[00196] The stress profile of the glass-based articles of Examples 5A and 5B are shown in Figure 20. A shown in Figure 20, Comparative Example 5A exhibited a known stress profile, whereas, Example 5B showed a stress profile according to one or more embodiments of this disclosure. The stored tensile energy of the glass-based articles of Examples 5A and 5B was calculated from the measured SCALP stress profile data and using equation (3) above. . The

calculated stored tensile energy is plotted as a function of measured CT (MPa), as shown in Figure 21.

[00197] As shown in Figure 21, Comparative 5A exhibited much greater stored tensile energy values for a given CT value than Example 5B (for the same CT value). Specifically, at a CT of about 55 MPa, Comparative Example 5A exhibited a stored tensile energy of about 8 J/m^2, whereas Example 5B exhibited a stored tensile energy of about 3.5 J/m^2. Comparative Example 8A and Example 5B were fractured and Example 5B fractured into fewer pieces than Comparative Example 5A, which fractured into a significantly greater number of pieces. Accordingly, without being bound by theory, it is believed that controlling the stored tensile energy may provide a way to control or predict fragmentation patterns or the number of fragments that result from fracture.

[00198] Glass substrates having a nominal composition as shown in Table 8 and having a thicknesses of about 1 mm each were subjected to chemical strengthening in a molten salt bath including $NaNO_3$ and a temperature of 430 °C for 4 hours (Comparative Example 5C) and for 61.5 hours (Example 5D). Comparative Example 5C exhibited a known stress profile, whereas, Example 5D showed a stress profile according to one or more embodiments of this disclosure. The stored tensile energy of Examples 5C and 5D was calculated using the same method used with Examples 5A-5B and plotted as a function of measured CT (MPa), as shown in Figure 22.

[00199] As shown in Figure 22, Comparative 5C exhibited much greater stored tensile energy values for a given CT value than Example 5D (for the same CT value). Comparative Example 5C and Example 5D were fractured and Example 5D fractured into fewer pieces than Comparative Example 5C, which fractured into a significantly greater number of pieces.

[00200] It will be apparent to those skilled in the art that various modifications and variations can be made without departing from the spirit or scope of the invention.

What is claimed is:

1. A glass-based article comprising:

a first surface and a second surface opposing the first surface defining a thickness (*t*);

a concentration of a metal oxide that is both non-zero and varies along a thickness range from about 0•*t* to about 0.3•*t*; and

a central tension (CT) region comprising a maximum CT of less than about 80 MPa,

wherein, when the glass-based article is fractured, the glass-based article fractures into at least 2 fragments/inch^2.

2. The glass-based article of claim 1, wherein the concentration of the metal oxide is non-zero and varies along the entire thickness.

3. The glass-based article of claim 1, wherein the metal oxide generates a stress along the thickness range.

4. The glass-based article of claim 1, wherein the concentration of the metal oxide decreases from the first surface to a point between the first surface and the second surface and increases from the point to the second surface.

5. The glass-based article of claim 1, further comprising a surface compressive stress (CS) of about 300 MPa or greater.

6. The glass-based article of claim 5, wherein the surface CS is about 500 MPa or greater.

7. The glass-based article of claim 1, wherein the concentration of the metal oxide is about 0.05 mol% or greater throughout the thickness.

8. The glass-based article of claim 1, wherein the concentration of the metal oxide at the first surface is about 1.5 times greater than the concentration of the metal oxides at a depth equal to about 0.5•*t*.

9. The glass-based article of claim 1, wherein the glass-based article comprises a total concentration of the metal oxide in the range from about 1 mol% to about 15 mol%.

10. The glass-based article of claim 1, wherein the metal oxide comprises any one or more of Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O.

11. The glass-based article of claim 1, further comprising a surface CS of about 200 MPa or greater and a chemical depth of layer of about 0.4•*t* or greater.

12. The glass-based article of claim 1, further comprising a CS extending from the first surface to a DOC, wherein the DOC is about 0.1•*t* or greater.

13. The glass-based article of claim 1, wherein the CT region comprises the metal oxide concentration gradient.

14. The glass-based article of claim 11, wherein the ratio of maximum CT to surface CS is in the range from about 0.01 to about 0.2.

15. The glass-based article of claim 1, wherein *t* comprises about 3 millimeters or less or about 1 millimeter or less.

16. The glass-based article of claim 1, further comprising an amorphous structure.

17. The glass-based article of claim 1, further comprising a crystalline structure.

18. The glass-based article of claim 1, further exhibiting a transmittance of about 88% or greater over a wavelength in the range from about 380 nm to about 780 nm.

19. The glass-based article of claim 1, further exhibiting CIELAB color space coordinates, under a CIE illuminant F02, of L* values of about 88 and greater, a* values in the range from about -3 to about +3, and b* values in the range from about -6 to about +6.

20. A glass-based article of claim 1, further comprising:

a first metal oxide concentration and a second metal oxide concentration,

wherein the first metal oxide concentration is in the range from about 0 mol% to about 15 mol% from a first thickness range from about 0•*t* to about 0.5•*t*, and

wherein the second metal oxide concentration is in the range from about 0 mol% to about 10 mol% from a second thickness range from about 0 micrometers to about 25 micrometers.

21. The glass-based article of claim 20, further comprising a third metal oxide.

22. The glass-based article of claim 1, further comprising a Young's modulus of less than 80 GPa.

23. The glass-based article of claim 1, further comprising a liquidus viscosity of about 100 kilopoise (kP) or greater.

24. The glass-based article of claim 1, further comprising any one or more of:

a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%,
a composition comprising greater than about 4 mol% Na_2O,
a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and
a composition comprising a non-zero amount of P_2O_5.

25. A glass-based article comprising:

a first surface and a second surface opposing the first surface defining a thickness (t) of about less than about 3 millimeters; and

a stress profile extending along the thickness,

wherein all points of the stress profile between a thickness range from about 0•t up to 0.3•t and from greater than 0.7•t, comprise a tangent that is less than about -0.1 MPa/micrometers or greater than about 0.1 MPa/micrometers,

wherein the stress profile comprises a maximum CS, a DOC and a maximum CT of less than about 80 MPa, wherein the ratio of maximum CT to maximum CS is in the range from about 0.01 to about 0.2 and wherein the DOC is about 0.1•t or greater, and

wherein, when the glass-based article is fractured, the glass-based article fractures into at least 2 fragments/inch^2.

26. The glass-based article of claim 25, further comprising a surface CS of about 300 MPa or greater.

27. The glass-based article of claim 25, further comprising a surface CS of about 200 MPa or greater and a chemical depth of layer (DOL) of about 0.4•*t* or greater.

28. The glass-based article of claim 25, further comprising a CS layer extending from the first surface to a DOC, wherein the DOC is about 0.1•*t* or greater.

29. The glass-based article of claim 25, further comprising a CT region, wherein the CT region comprises a metal oxide concentration gradient.

30. The glass-based article of claim 26, further comprising ratio of maximum CT to surface CS in the range from about 0.01 to about 0.2.

31. The glass-based article of claim 25, further comprising a Young's modulus of less than 80 GPa.

32. The glass-based article of claim 25, further comprising a liquidus viscosity of about 100 kP or greater.

33. The glass-based article of claim 25, further comprising any one or more of:

a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%,

a composition comprising greater than about 4 mol% Na_2O,

a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and

a composition comprising a non-zero amount of P_2O_5.

34. A glass-based article comprising:

a first surface and a second surface opposing the first surface defining a thickness (*t*); and

a concentration of a metal oxide that is both non-zero and varies along a thickness range from about 0•*t* to about 0.3•*t*;

a surface compressive stress of greater than about 200MPa or greater; and

a CT region having a maximum CT of less than about 80 MPa.

35. The glass-based article of claim 34, wherein the thickness range is from about 0•*t* to about 0.4•*t*.

36. The glass-based article of claim 34, wherein the thickness range is from about 0•*t* to about 0.45•*t*.

37. The glass-based article of claim 34, wherein the metal oxide generates a stress along the thickness range.

38. The glass-based article of claim 37, wherein the metal oxide has a largest ionic diameter of all of the total metal oxides in the glass-based substrate.

39. The glass-based article of claim 34, wherein the concentration of the metal oxide decreases from the first surface to a point between the first surface and the second surface and increases from the point to the second surface.

40. The glass-based article of claim 34, wherein, when the glass-based article is fractured, the glass-based article fractures into at least 1 fragment/inch^2 up to 40 fragments/inch^2.

41. The glass-based article of claim 34, wherein the glass-based article comprises a diffusivity of about 450 μm^2/hour or greater at about 460 °C and a DOC greater than about 0.15•*t*, and wherein the surface CS is 1.5 times the maximum CT or greater.

42. The glass-based article of claim 34, wherein the glass-based article comprises a fracture toughness (K_{1C}) of about 0.7 MPa·m$^{1/2}$ or greater.

43. The glass-based article of claim 41, wherein the surface CS is greater than the maximum CT.

44. The glass-based article of claim 34, wherein the surface CS of about 300 MPa or greater and a thickness of about 2 millimeters or less.

45. The glass-based article of claim 34, wherein the concentration of the metal oxide is about 0.05 mol% or greater throughout the thickness.

46. The glass-based article of claim 34, wherein the concentration of the metal oxide at the first surface is about 1.5 times greater than the concentration of the metal oxides at a depth equal to about $0.5 \cdot t$.

47. The glass-based article of claim 34, wherein the total concentration of the metal oxide is in the range from about 1 mol% to about 15 mol%.

48. The glass-based article of claim 34, further comprising a chemical depth of layer of about $0.4 \cdot t$ or greater.

49. The glass-based article of claim 34, further comprising a CS layer extending from the first surface to a DOC, wherein the DOC is about $0.1 \cdot t$ or greater.

50. The glass-based article of claim 34, wherein the CT region comprises the metal oxide concentration gradient.

51. The glass-based article of claim 34, wherein the ratio of maximum CT to surface CS is in the range from about 0.01 to about 0.2.

52. The glass-based article of claim 34, wherein *t* comprises about 1 millimeter or less.

53. The glass-based article of claim 34, further comprising a Young's modulus of less than 80 GPa.

54. The glass-based article of claim 34, further comprising a liquidus viscosity of about 100 kP or greater.

55. The glass-based article of claim 34, further comprising any one or more of:

a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%,

a composition comprising greater than about 4 mol% Na_2O,

a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and

a composition comprising a non-zero amount of P_2O_5.

56. A glass-based article comprising:

a first surface and a second surface opposing the first surface defining a thickness (t); and

a metal oxide that forms a concentration gradient,

wherein the concentration of the metal oxide decreases from the first surface to a point between the first surface and the second surface and increases from the point to the second surface,

wherein the concentration of the metal oxide at the point is non-zero, and

wherein the glass-based article comprises a stored tensile energy of about greater than 0 J/m2 to less than 20 J/m^2 and an elastic modulus of less than about 80 GPa.

57. The glass-based article of claim 56, further comprising a surface CS of about 300 MPa or greater.

58. The glass-based article of claim 56 wherein the concentration of the metal oxide is about 0.05 mol% or greater throughout the thickness.

59. The glass-based article of claim 56, wherein the concentration of the metal oxide at the first surface is about 1.5 times greater than the concentration of the metal oxides at a depth equal to about 0.5•t.

60. The glass-based article of claim 56, wherein the total concentration of the metal oxide is in the range from about 1 mol% to about 15 mol%.

61. The glass-based article of claim 56, wherein the metal oxide comprises any one or more of Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O.

62. The glass-based article of claim 56, further comprising a CS layer extending from the first surface to a DOC, wherein the DOC is about 0.1•*t* or greater.

63. The glass-based article of claim 56, further comprising a CT region, wherein the CT region comprises the metal oxide concentration gradient.

64. The glass-based article of claim 63, wherein the CT region comprises a maximum CT and the ratio of maximum CT to surface CS is in the range from about 0.01 to about 0.2.

65. The glass-based article of claim 56, wherein *t* comprises about 3 millimeters or less.

66. The glass-based article of claim 64, wherein the maximum CT is less than about 80 MPa.

67. The glass-based article of claim 56 further comprising a liquidus viscosity of about 100 kP or greater.

68. The glass-based article of claim 56, further comprising any one or more of:

a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%,

a composition comprising greater than about 4 mol% Na_2O,

a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and

a composition comprising a non-zero amount of P_2O_5.

69. A glass-based article comprising:

a first surface and a second surface opposing the first surface defining a thickness (*t*) of about less than about 3 millimeter; and

a stress profile extending along the thickness,

wherein all points of the stress profile between a thickness range from about 0*t* up to 0.3*t* and from greater than 0.7*t*, comprise a tangent that is less than about -0.1 MPa/micrometers or greater than about 0.1 MPa/micrometers,

wherein the stress profile comprises a maximum CS, a DOC and a maximum CT, wherein the ratio of maximum CT to maximum CS is in the range from about 0.01 to about 0.2 and wherein the DOC is about 0.1•*t* or greater, and

wherein the glass-based article comprises a stored tensile energy of about greater than 0 J/m^2 to less than 20 J/m^2 and an elastic modulus of less than about 80 GPa.

70. The glass-based article of claim 69, further comprising a non-zero concentration of a metal oxide that continuously varies along the entire thickness.

71. The glass-based article of claim 69, further comprising a non-zero concentration of a metal oxide that continuously varies along thickness segments of less than about 10 micrometers.

72. The glass-based article of claim 69, wherein the maximum CS comprises about 300 MPa or greater.

73. The glass-based article of claim 69, further comprising a chemical depth of layer of about 0.4•*t* or greater.

74. The glass-based article of claim 69, further comprising a CT region, wherein the CT region comprises the metal oxide concentration gradient.

75. The glass-based article of claim 69, wherein *t* comprises about 1 millimeters or less.

76. The glass-based article of claim 64, wherein the maximum CT is less than about 80 MPa.

77. The glass-based article of claim 56 further comprising a liquidus viscosity of about 100 kP or greater.

78. The glass-based article of claim 56, further comprising any one or more of:

a composition comprising a combined amount of Al_2O_3 and Na_2O of greater than about 15 mol%,

a composition comprising greater than about 4 mol% Na_2O,

a composition substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO, and

a composition comprising a non-zero amount of P_2O_5.

79. A glass-based article comprising:

a stress profile including a CS region and a CT region, wherein the CT region is defined by the equation Stress(x) = MaxCT – (((MaxCT • (n+1))/0.5^n)•|(x/t)-0.5|^n),

wherein MaxCT is a maximum CT value and provided as a positive value in units of MPa, x is position along the thickness (*t*) in micrometers, and n is between 1.5 and 5.

80. The glass-based article of claim 79, wherein the CT region comprises a maximum CT value in the range from about 50 MPa to about 250 MPa and the maximum CT value is at a depth in the range from about 0.4*t* to about 0.6*t*.

81. The glass-based article of claim 79, wherein, from a thickness in the range from about 0*t* to about 0.1*t* microns, the stress profile comprises a slope in the range from about 20 MPa/microns to about 200 MPa/microns.

82. The glass-based article of claim 79, wherein the stress profile is defined by a plurality of error functions as measured from 0.5t to the surface.

83. A use of a glass composition in a strengthened glass-based article, the glass composition comprising (in mol%):

SiO_2 in an amount in the range from about 60 to about 75;

Al_2O_3 in an amount in the range from about 12 to about 20;

B_2O_3 in an amount in the range from about 0 to about 5;

Li_2O in an amount in the range from about 2 to about 8;

Na_2O in an amount greater than 4;

P_2O_5 in a non-zero amount;

MgO in an amount in the range from about 0 to about 5;

ZnO in an amount in the range from about 0 to about 3;

CaO in an amount in the range from about 0 to about 5,

wherein the glass composition is ion-exchangeable and is amorphous,
wherein the total amount of Al_2O_3 and Na_2O is greater than about 15 mol%,

wherein the glass composition is substantially free of nucleating agents, and

wherein the glass composition comprises a liquidus viscosity of about 100 kP or greater.

84. The use of a glass composition of claim 83, wherein the glass composition is substantially free of B_2O_3, ZnO, or both B_2O_3 and ZnO.

85. A glass substrate comprising a composition including, in mol%,

SiO_2 in an amount in the range from about 60 to about 75;
Al_2O_3 in an amount in the range from about 12 to about 20;
B_2O_3 in an amount in the range from about 0 to about 5;
Li_2O in an amount in the range from about 2 to about 8;
Na_2O in an amount greater than about 4;
MgO in an amount in the range from about 0 to about 5;
ZnO in an amount in the range from about 0 to about 3; CaO in an amount in the range from about 0 to about 5; and
P_2O_5 in a non-zero amount;

wherein the glass substrate is ion-exchangeable and is amorphous,
wherein total amount of Al_2O_3 and Na_2O in the composition is greater than about 15 mol%,
wherein the glass composition is substantially free of nucleating agents and comprises a liquidus viscosity of about 100 kP or greater.

86. A glass substrate comprising a composition including, in mol%,

SiO_2 in an amount in the range from about 60 to about 75;
Al_2O_3 in an amount in the range from about 12 to about 20;
B_2O_3 in an amount in the range from about 0 to about 5;
Li_2O in an amount in the range from about 2 to about 8;
Na_2O in an amount greater than about 4;
MgO in an amount in the range from about 0 to about 5;

ZnO in an amount in the range from about 0 to about 3; and

CaO in an amount in the range from about 0 to about 5,

wherein the glass substrate is amorphous and is strengthened,

wherein the Na_2O concentration varies,

wherein the composition is substantially free of nucleating agents,

total amount of Al_2O_3 and Na_2O in the composition is greater than about 15 mol%,

wherein the glass composition is substantially free of nucleating agents, and comprises a liquidus viscosity of about 100 kP or greater.

87. The glass substrate of claim 86, further comprising a non-zero amount of P_2O_5.

FUSION-FORMABLE, GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT

ABSTRACT

Embodiments of a glass-based article including a first surface and a second surface opposing the first surface defining a thickness (*t*) of about 3 millimeters or less (e.g., about 1 millimeter or less), and a stress profile, wherein all points of the stress profile between a thickness range from about 0•*t* up to 0.3•*t* and from greater than 0.7•*t*, comprise a tangent that is less than about -0.1 MPa/micrometers or greater than about 0.1 MPa/micrometers,, are disclosed. In some embodiments, the glass-based article includes a non-zero metal oxide concentration that varies along at least a portion of the thickness (e.g., 0•*t* to about 0.3•*t*) and a maximum central tension of less than about 80 MPa. In some embodiments, the concentration of metal oxide or alkali metal oxide decreases from the first surface to a point between the first surface and the second surface and increases from the point to the second surface. The concentration of the metal oxide may be about 0.05 mol% or greater or about 0.5 mol% or greater throughout the thickness. Methods for forming such glass-based articles are also disclosed.

FIG. 1 (PRIOR ART)

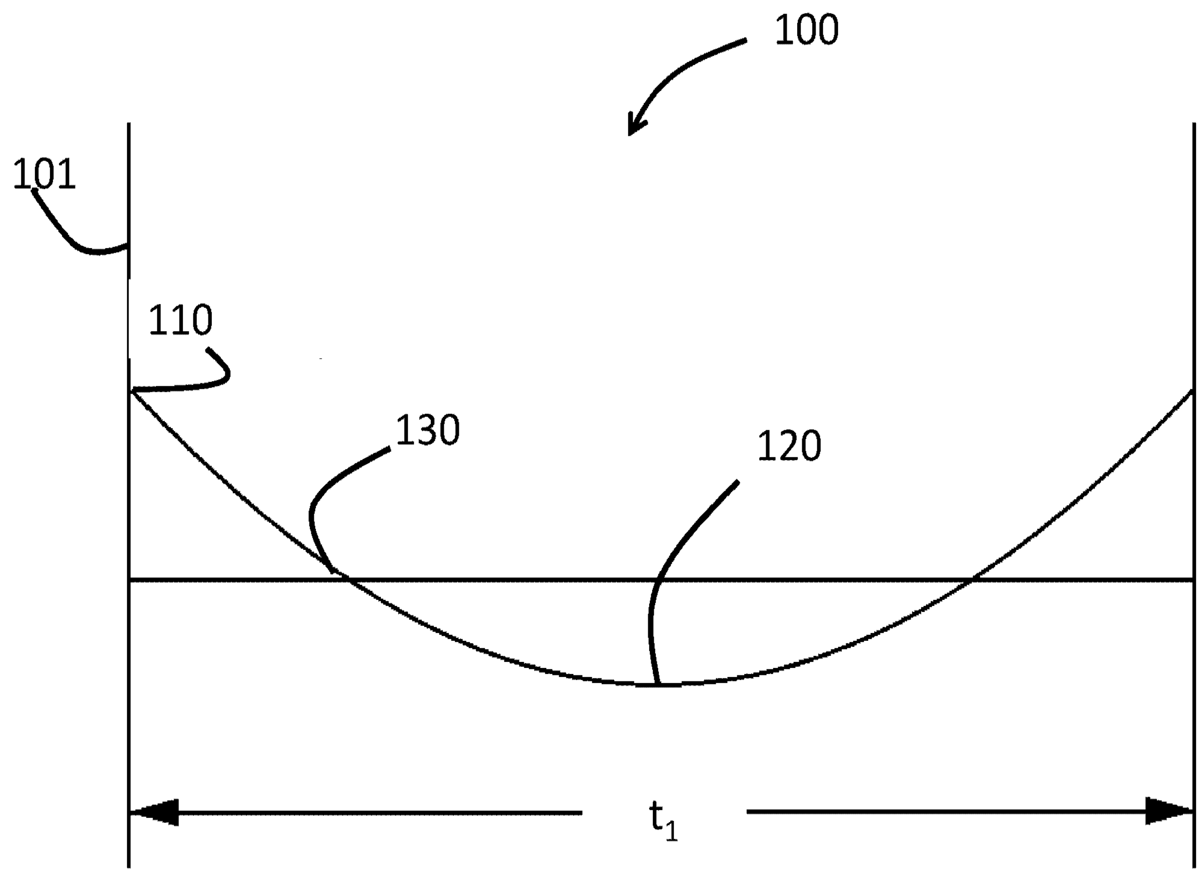

FIG. 2 (PRIOR ART)

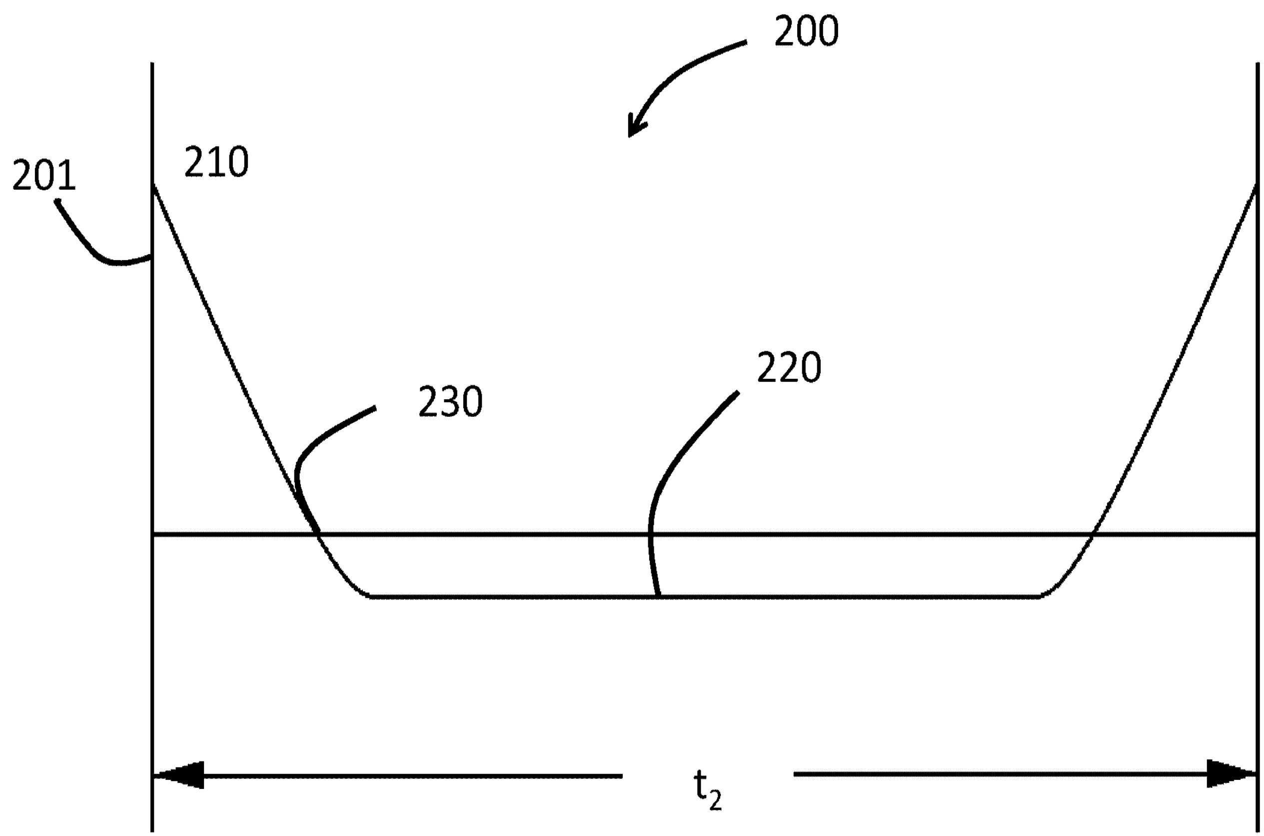

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FIG. 3

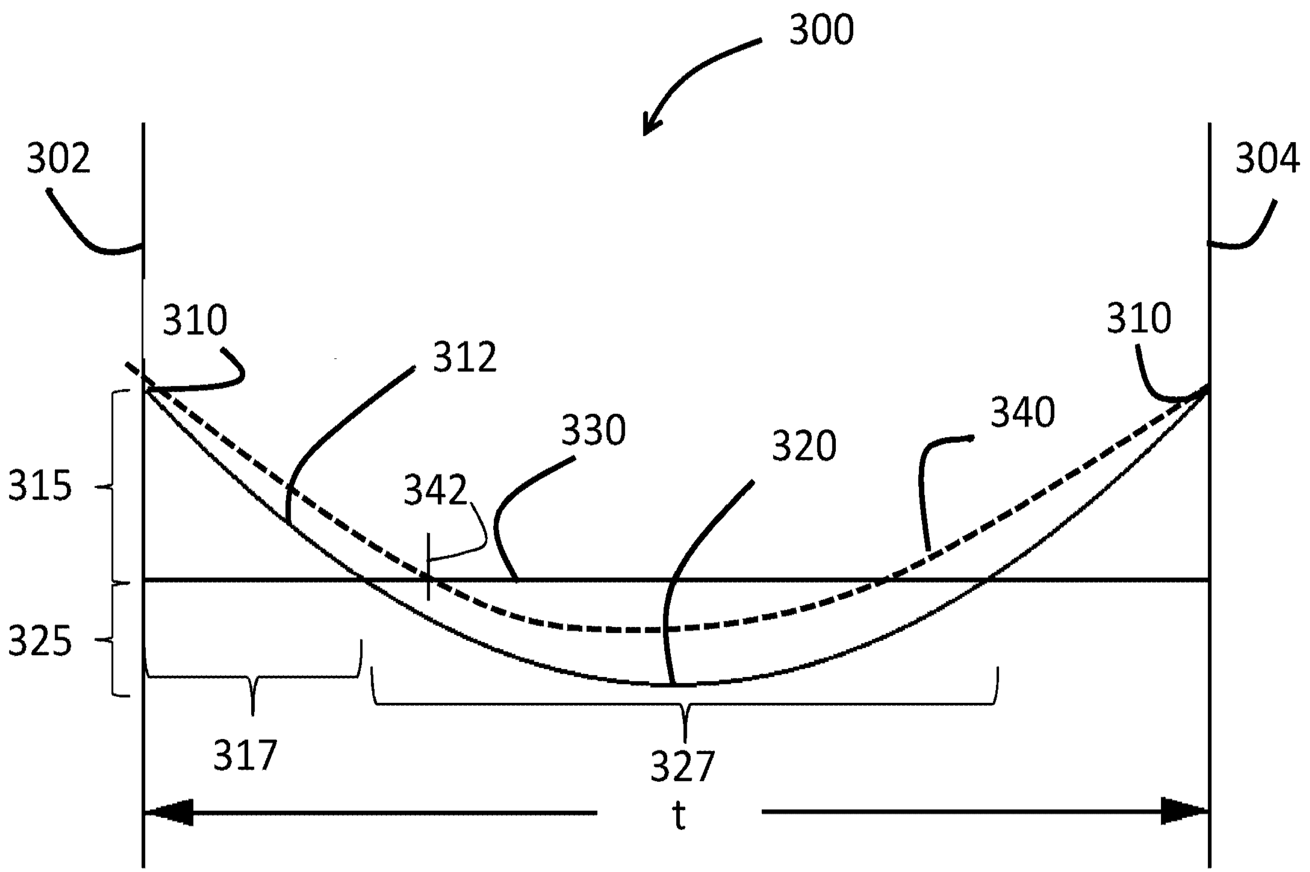

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FIG. 4

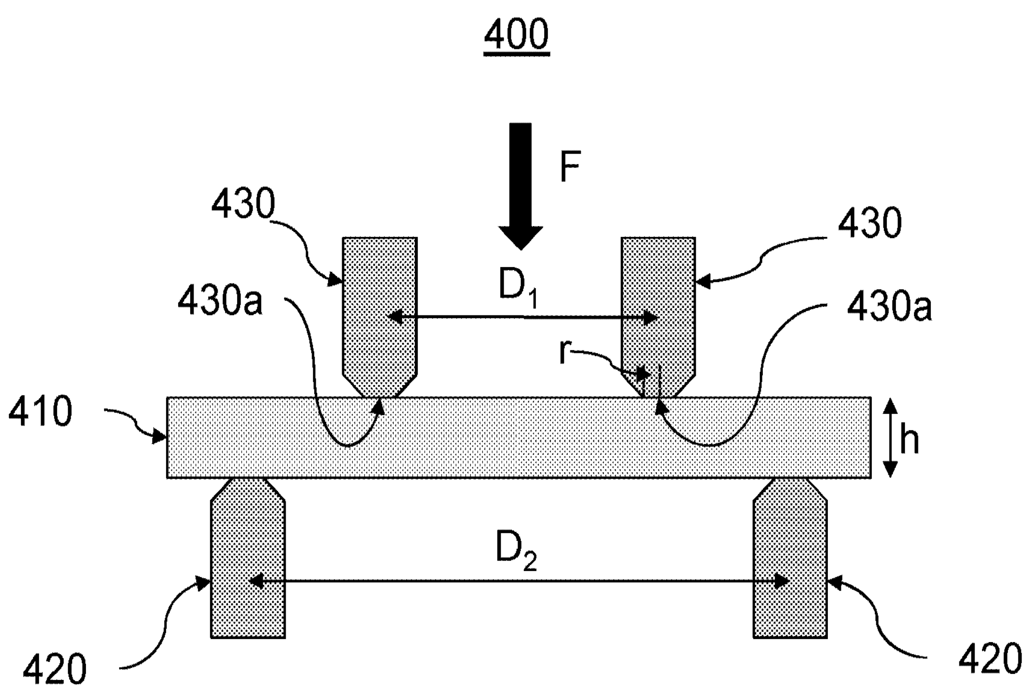


FIGURE 5

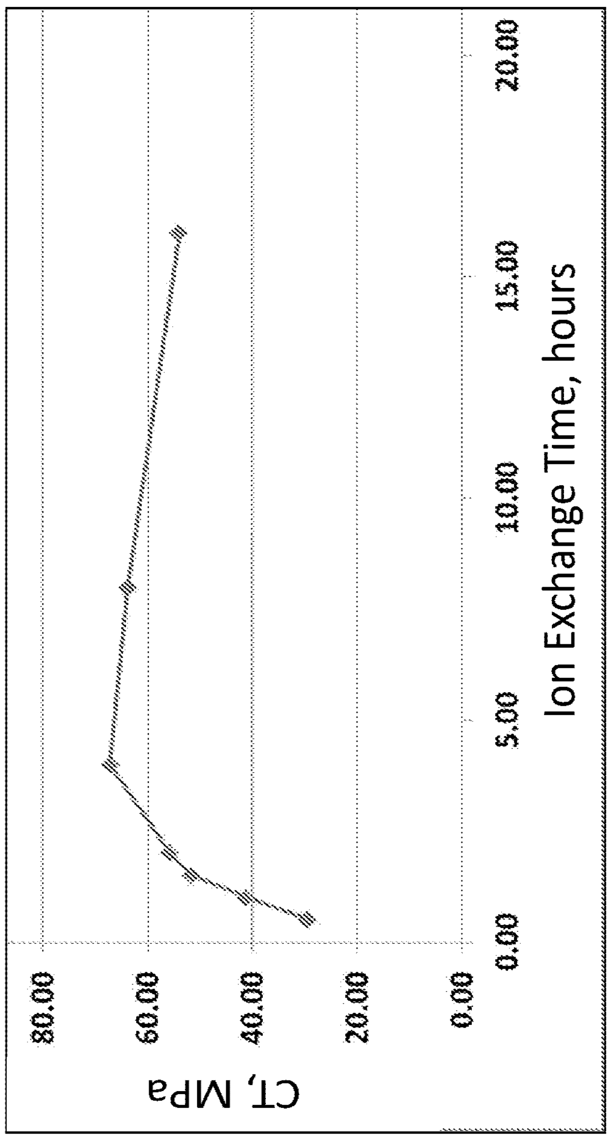

CT, MPa
80.00
60.00
40.00
20.00
0.00
0.00
5.00
10.00
15.00
20.00
Ion Exchange Time, hours

FIGURE 6

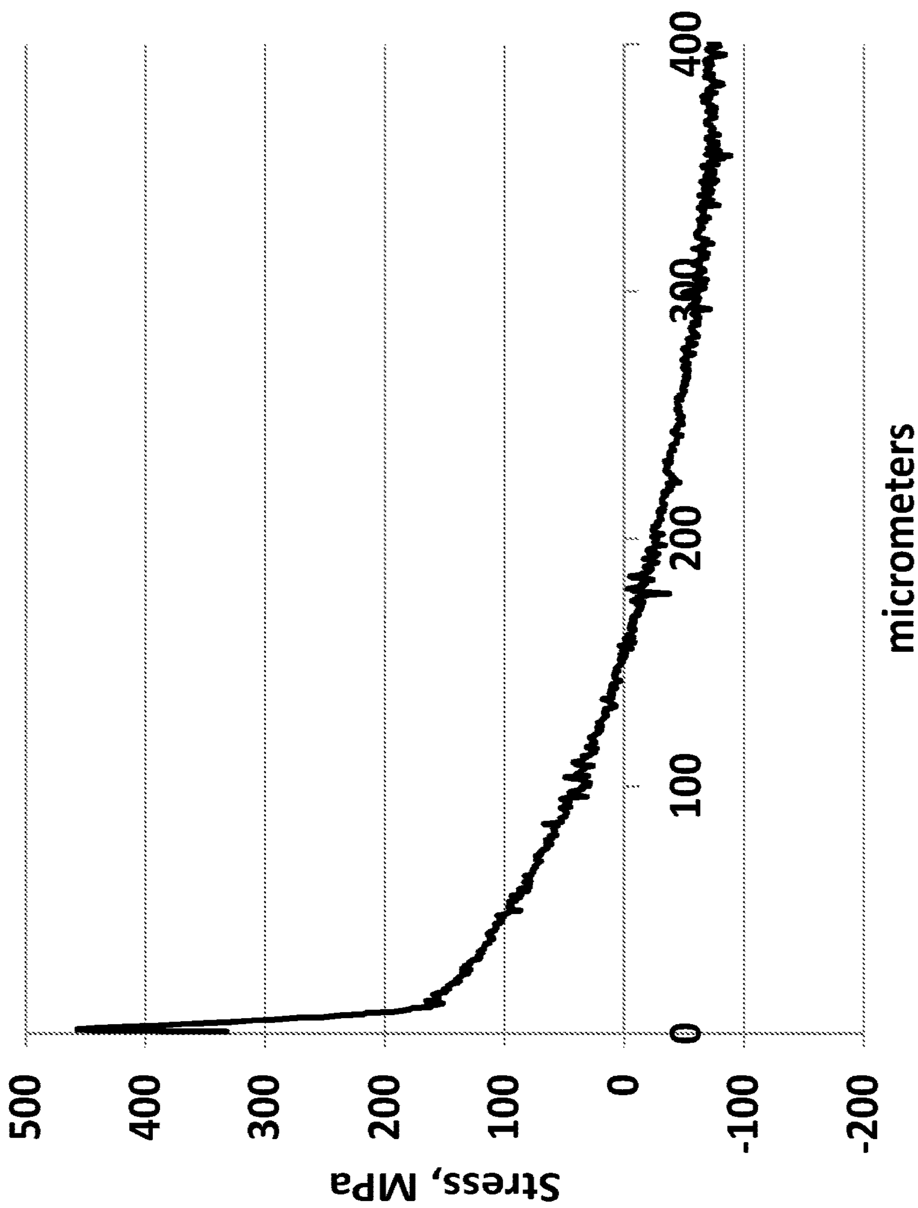
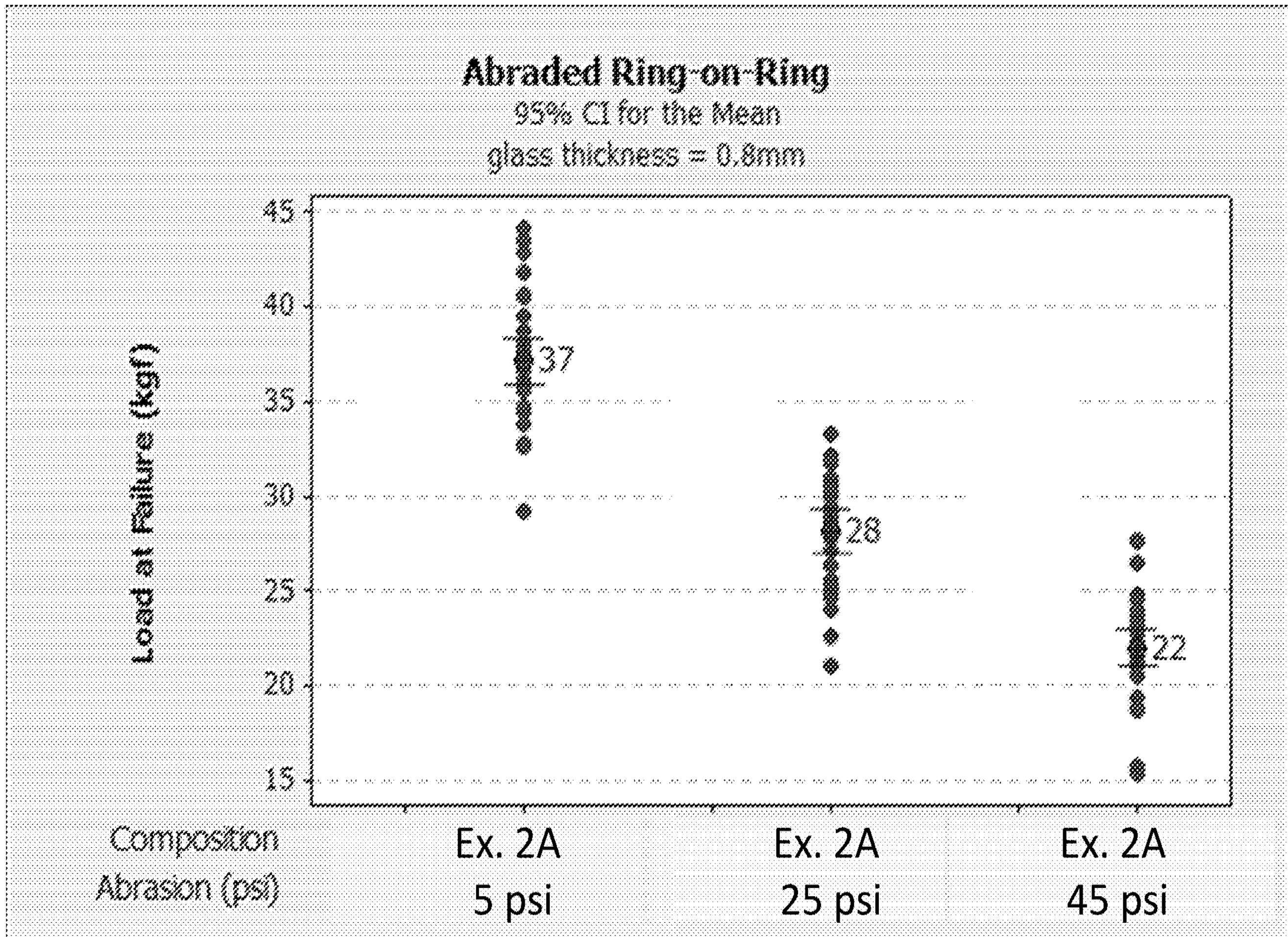

Stress, MPa
500
400
300
200
100
0
-100
-200
0
100
200
300
400
micrometers

FIGURE 7



Abraded Ring-on-Ring
95% CI for the Mean
glass thickness = 0.8mm
Load at Failure (kgf)
45
40
35
30
25
20
15
37
28
22
Composition
Abrasion (psi)
Ex. 2A
5 psi
Ex. 2A
25 psi
Ex. 2A
45 psi

FIGURE 8

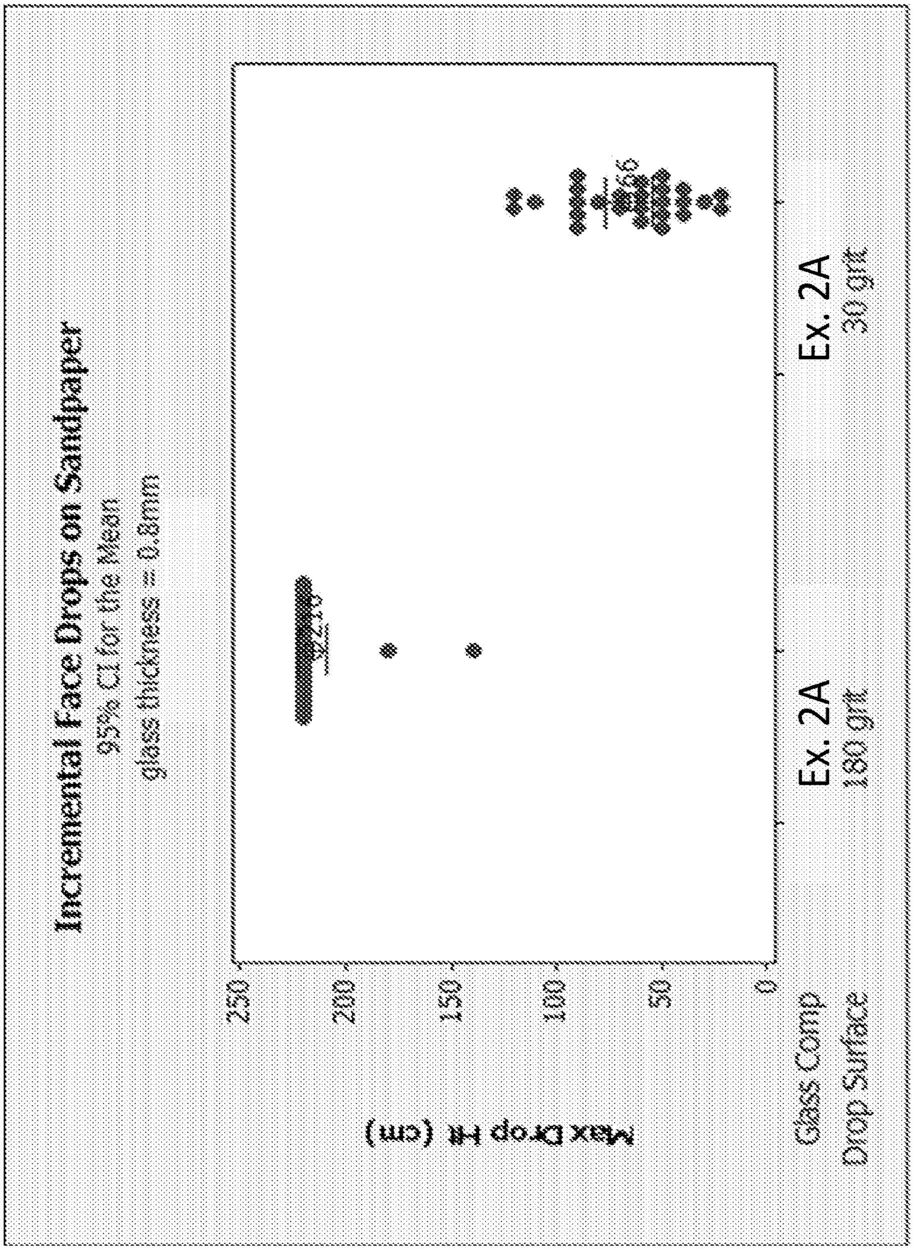
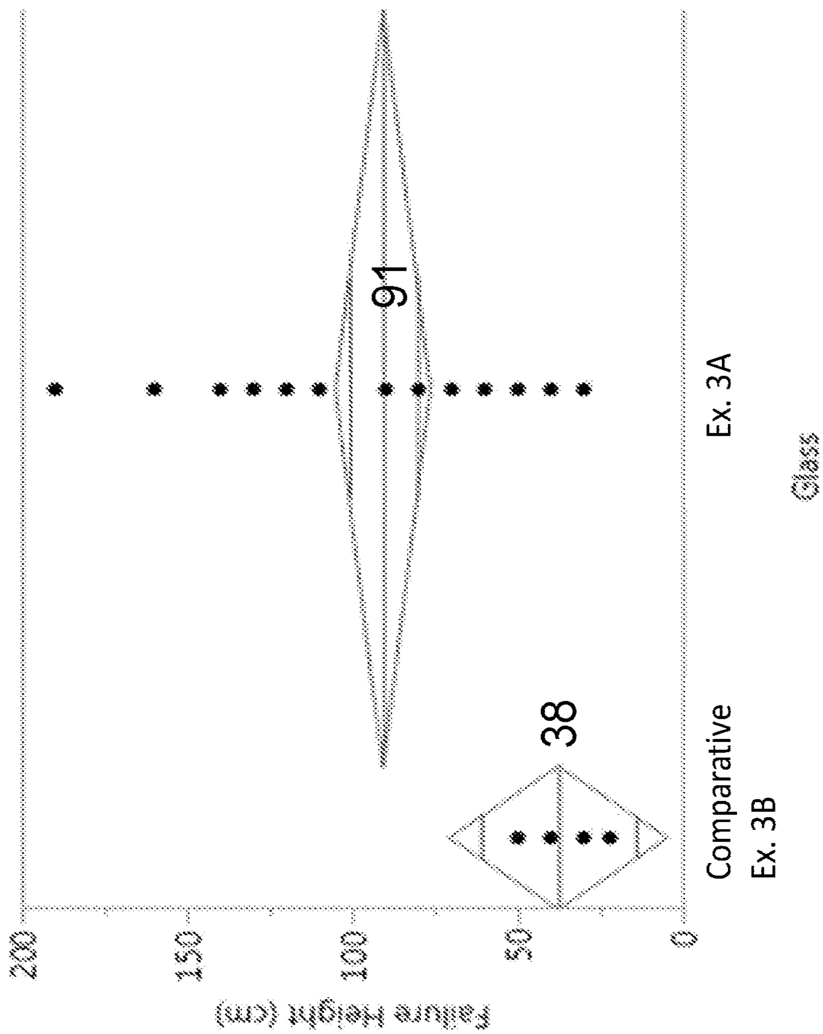

Incremental Face Drops on Sandpaper
95% CI for the Mean
glass thickness = 0.8mm
Max Drop Ht (cm)
250
200
150
100
50
0
Glass Comp
Drop Surface
Ex. 2A
180 grit
Ex. 2A
30 grit

FIGURE 9



Failure Height (cm)
200
150
100
50
0
91
38
Comparative
Ex. 3B
Ex. 3A
Glass

FIGURE 10

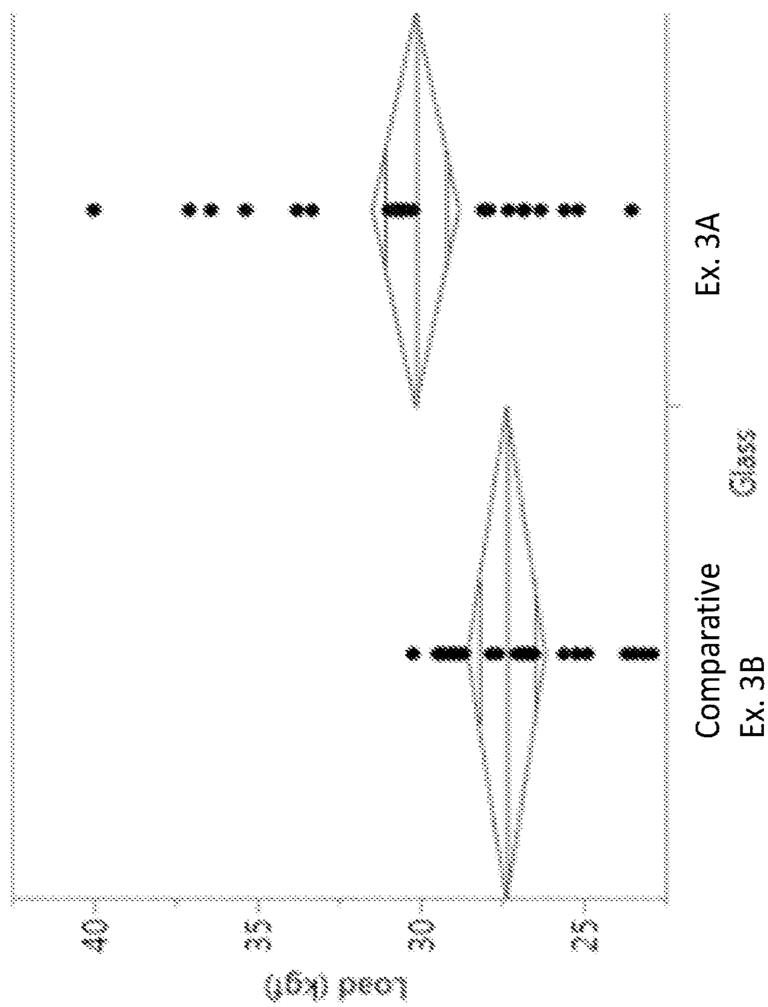


FIGURE 11

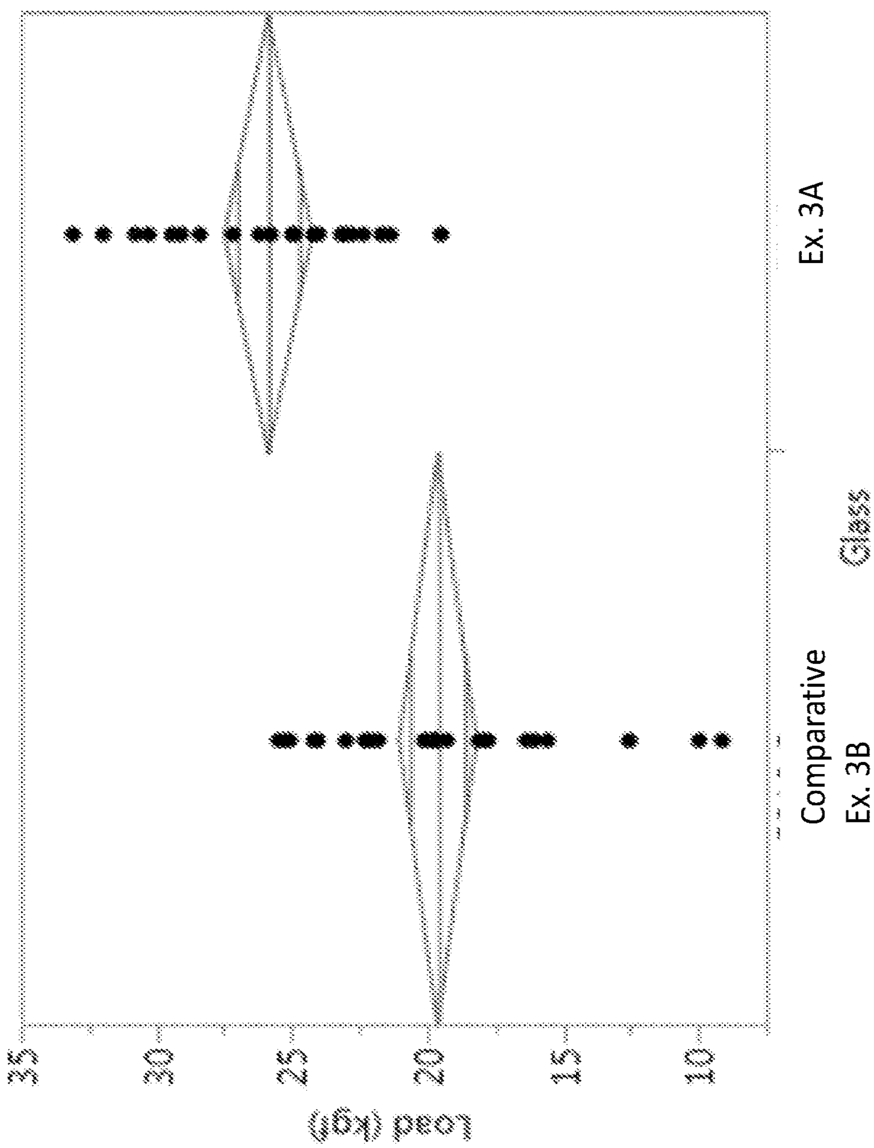


FIG. 12

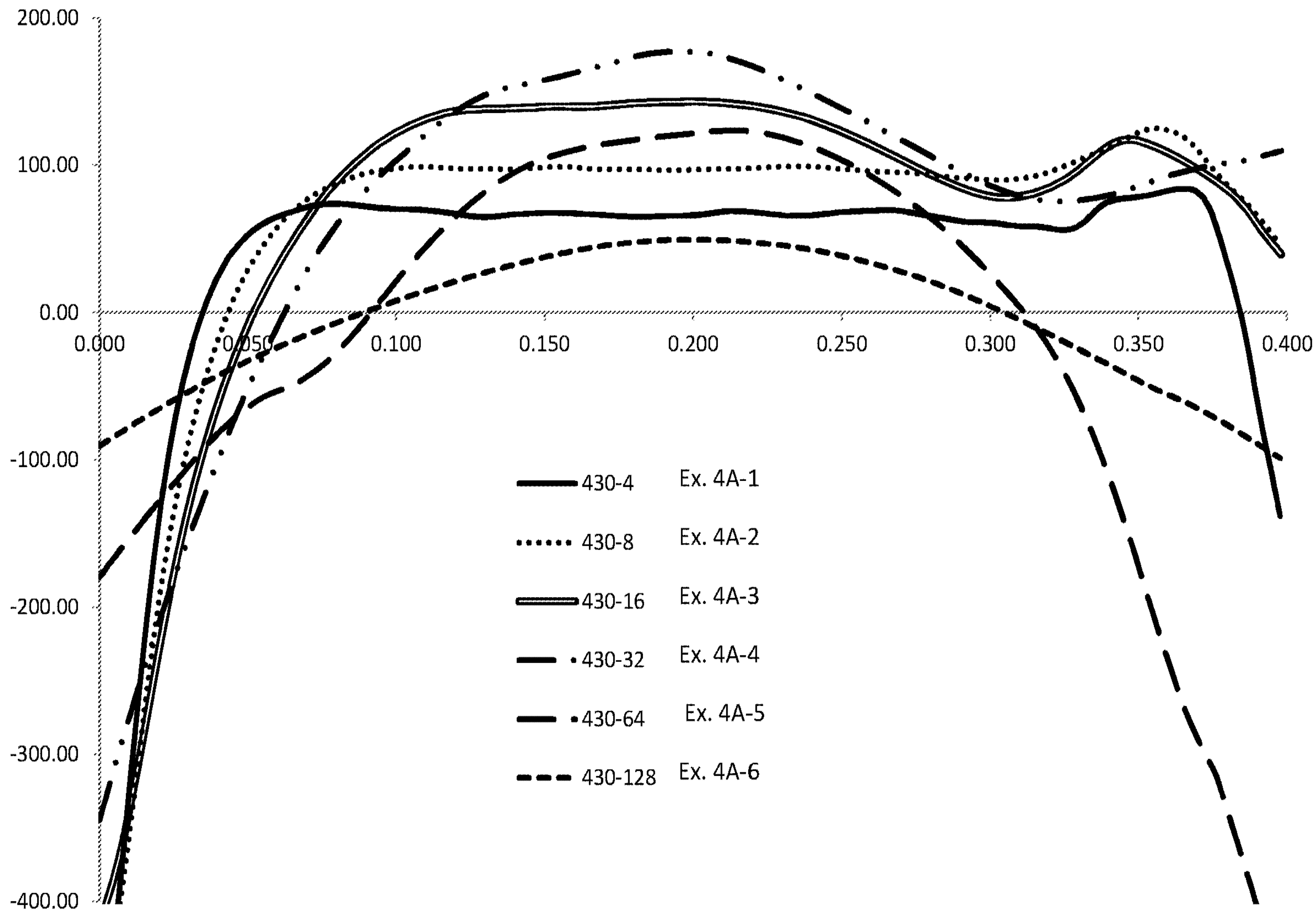

200.00
100.00
0.00
-100.00
-200.00
-300.00
-400.00
0.000
0.050
0.100
0.150
0.200
0.250
0.300
0.350
0.400
430-4 Ex. 4A-1
430-8 Ex. 4A-2
430-16 Ex. 4A-3
430-32 Ex. 4A-4
430-64 Ex. 4A-5
430-128 Ex. 4A-6

FIG. 13

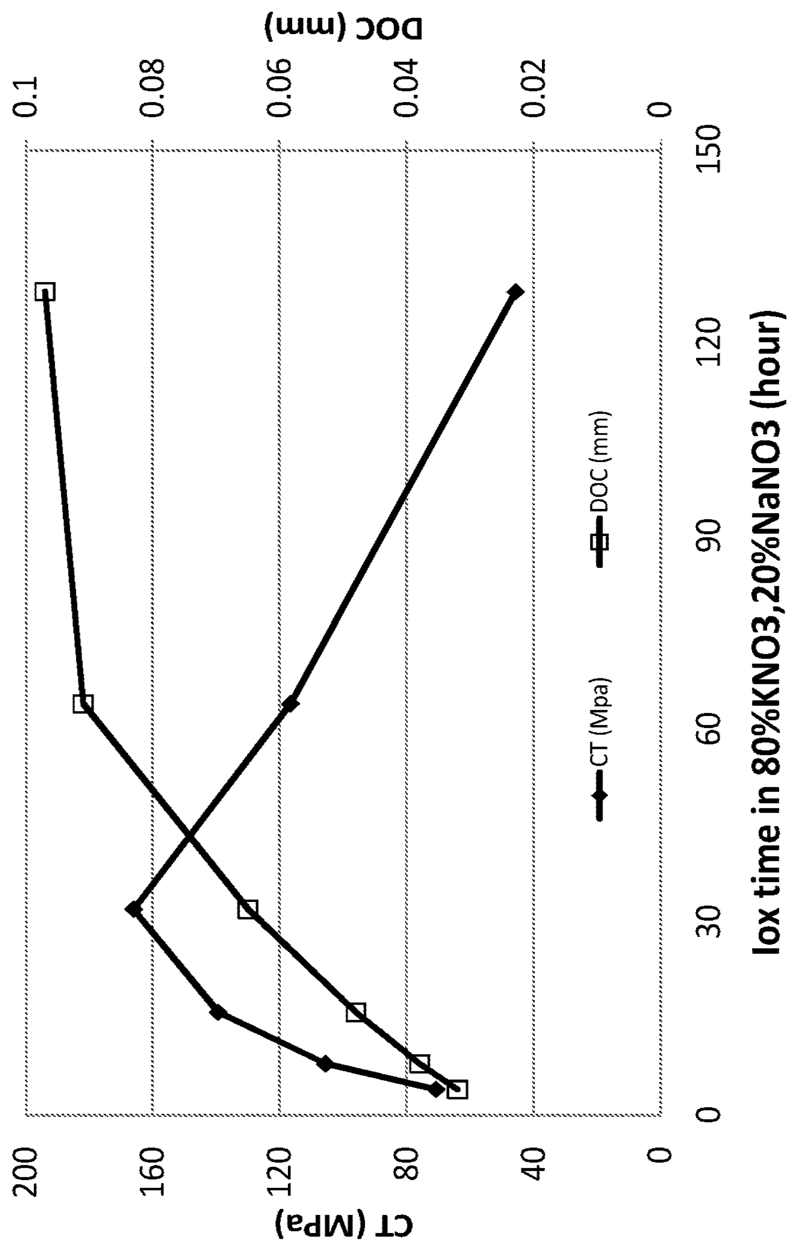

DOC (mm)
0.1
0.08
0.06
0.04
0.02
0
CT (MPa)
200
160
120
80
40
0
0
30
60
90
120
150
CT (Mpa)
DOC (mm)
Iox time in 80%KNO3,20%NaNO3 (hour)

FIG. 14

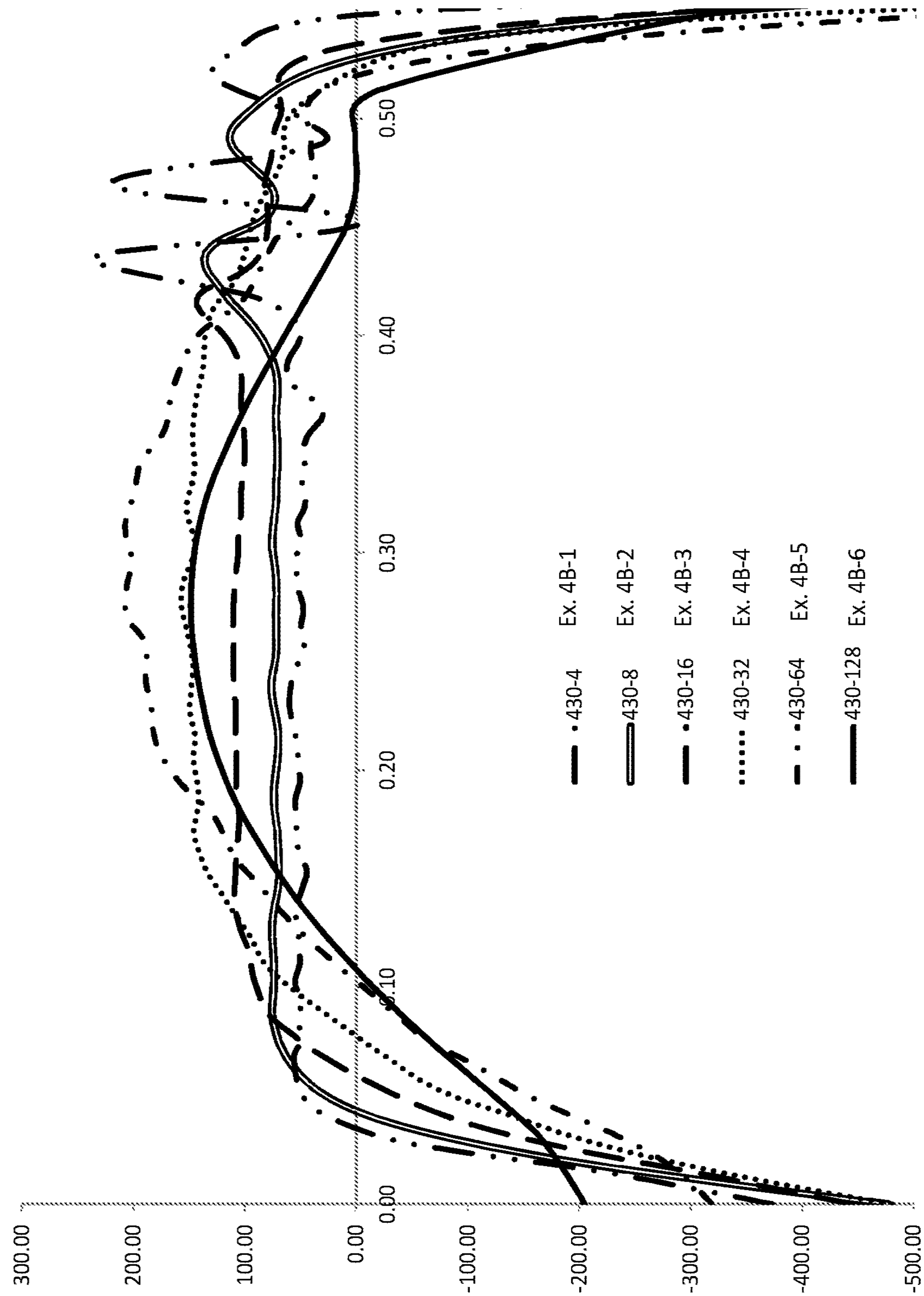
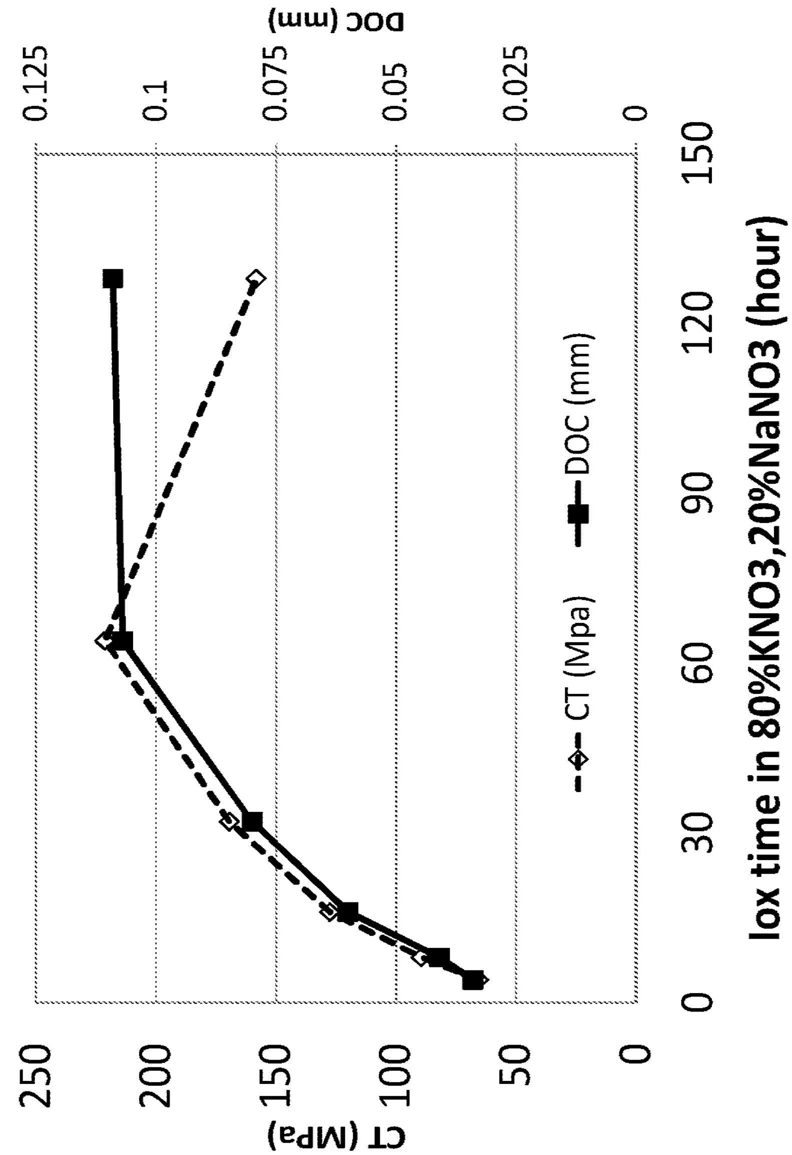

300.00
200.00
100.00
0.00
-100.00
-200.00
-300.00
-400.00
-500.00
0.00
0.10
0.20
0.30
0.40
0.50
430-4 Ex. 4B-1
430-8 Ex. 4B-2
430-16 Ex. 4B-3
430-32 Ex. 4B-4
430-64 Ex. 4B-5
430-128 Ex. 4B-6

FIG. 15



CT (MPa)
250
200
150
100
50
0
DOC (mm)
0.125
0.1
0.075
0.05
0.025
0
0
30
60
90
120
150
Iox time in 80%KNO3,20%NaNO3 (hour)
CT (Mpa)
DOC (mm)

16/22

FIG. 16

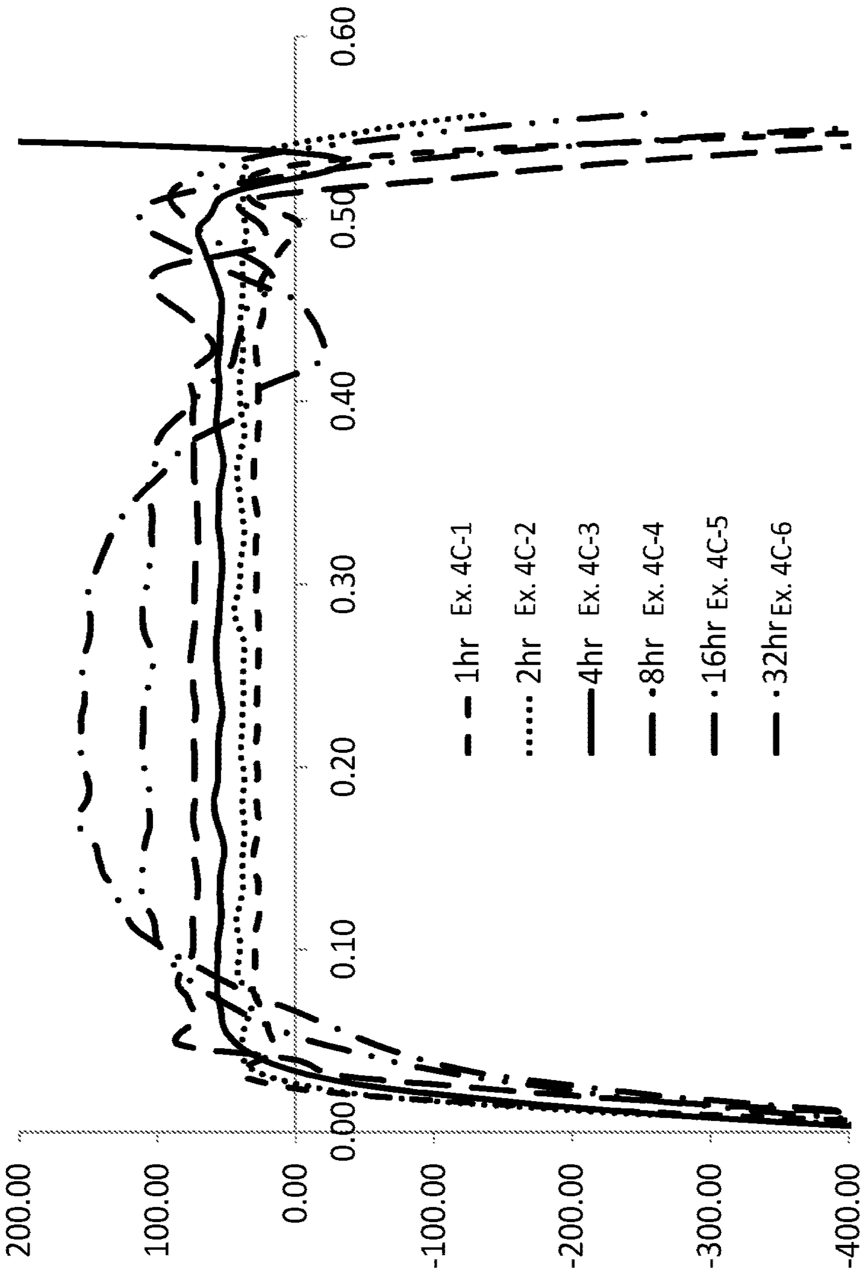

200.00
100.00
0.00
-100.00
-200.00
-300.00
-400.00
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1hr Ex. 4C-1
2hr Ex. 4C-2
4hr Ex. 4C-3
8hr Ex. 4C-4
16hr Ex. 4C-5
32hr Ex. 4C-6

FIG. 17

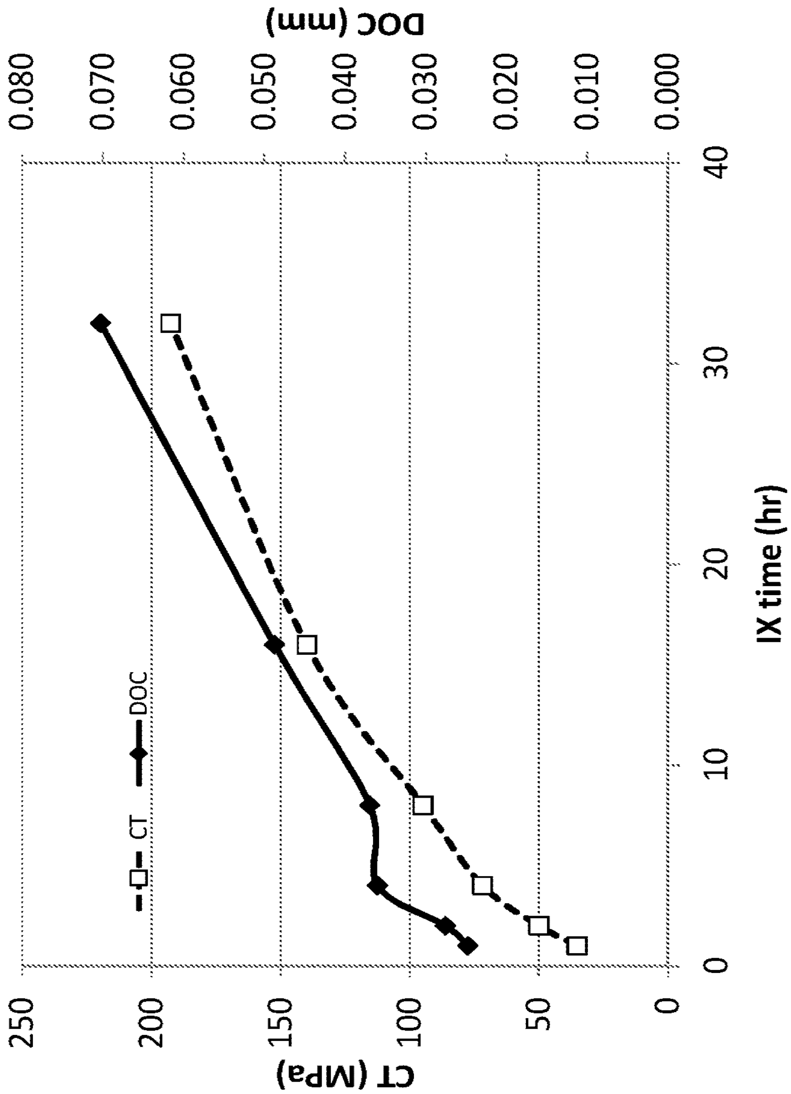

CT
DOC
CT (MPa)
250
200
150
100
50
0
DOC (mm)
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0
10
20
30
40
IX time (hr)

FIG. 18

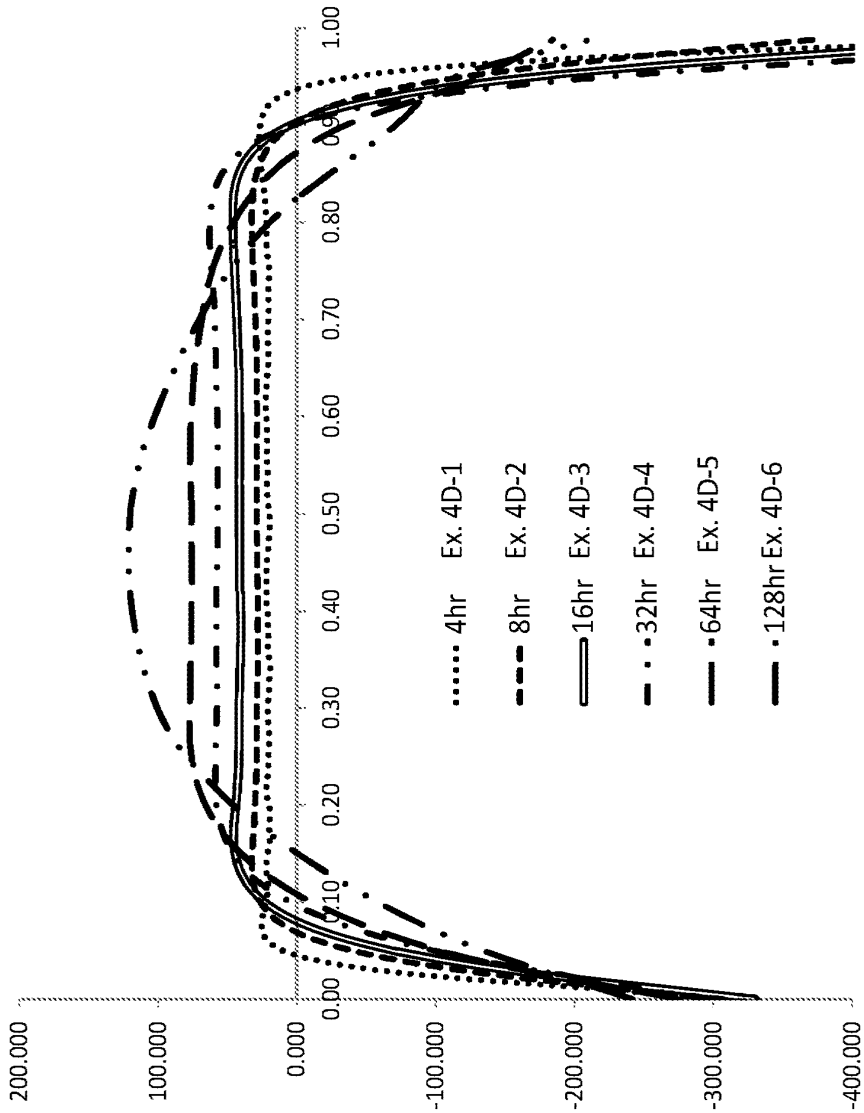
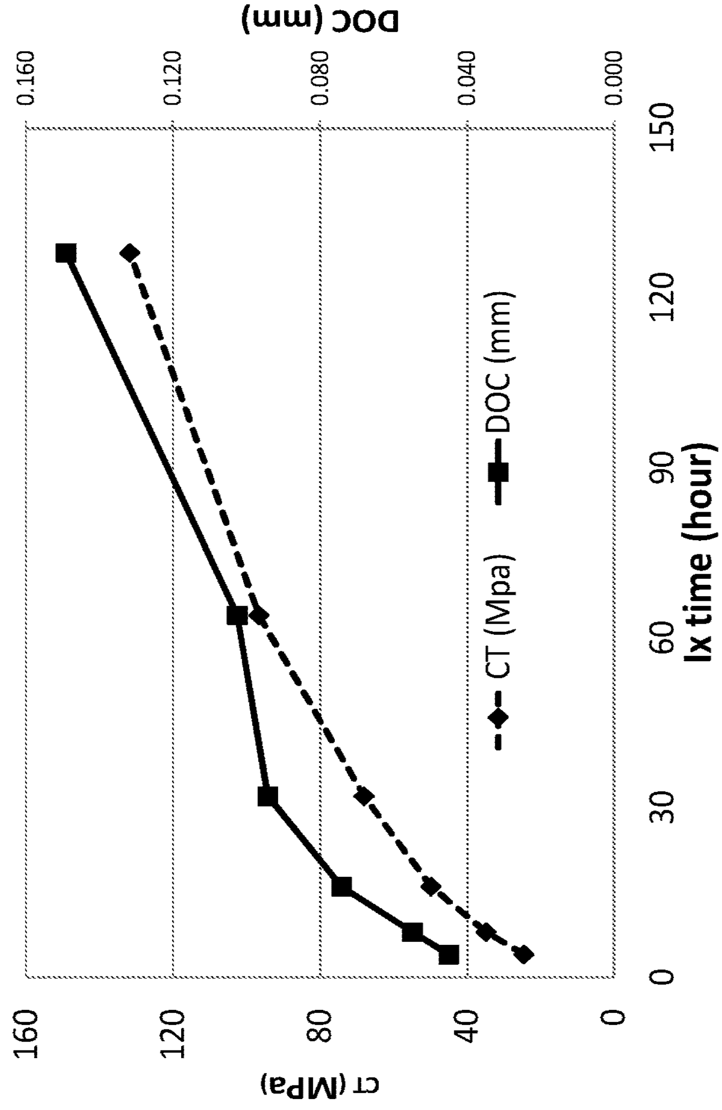

4hr Ex. 4D-1
8hr Ex. 4D-2
16hr Ex. 4D-3
32hr Ex. 4D-4
64hr Ex. 4D-5
128hr Ex. 4D-6
200.000
100.000
0.000
-100.000
-200.000
-300.000
-400.000
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00

FIG. 19



DOC (mm)
0.160
0.120
0.080
0.040
0.000
CT (Mpa)
DOC (mm)
160
120
80
40
0
CT (MPa)
0
30
60
90
120
150
Ix time (hour)

FIG. 20

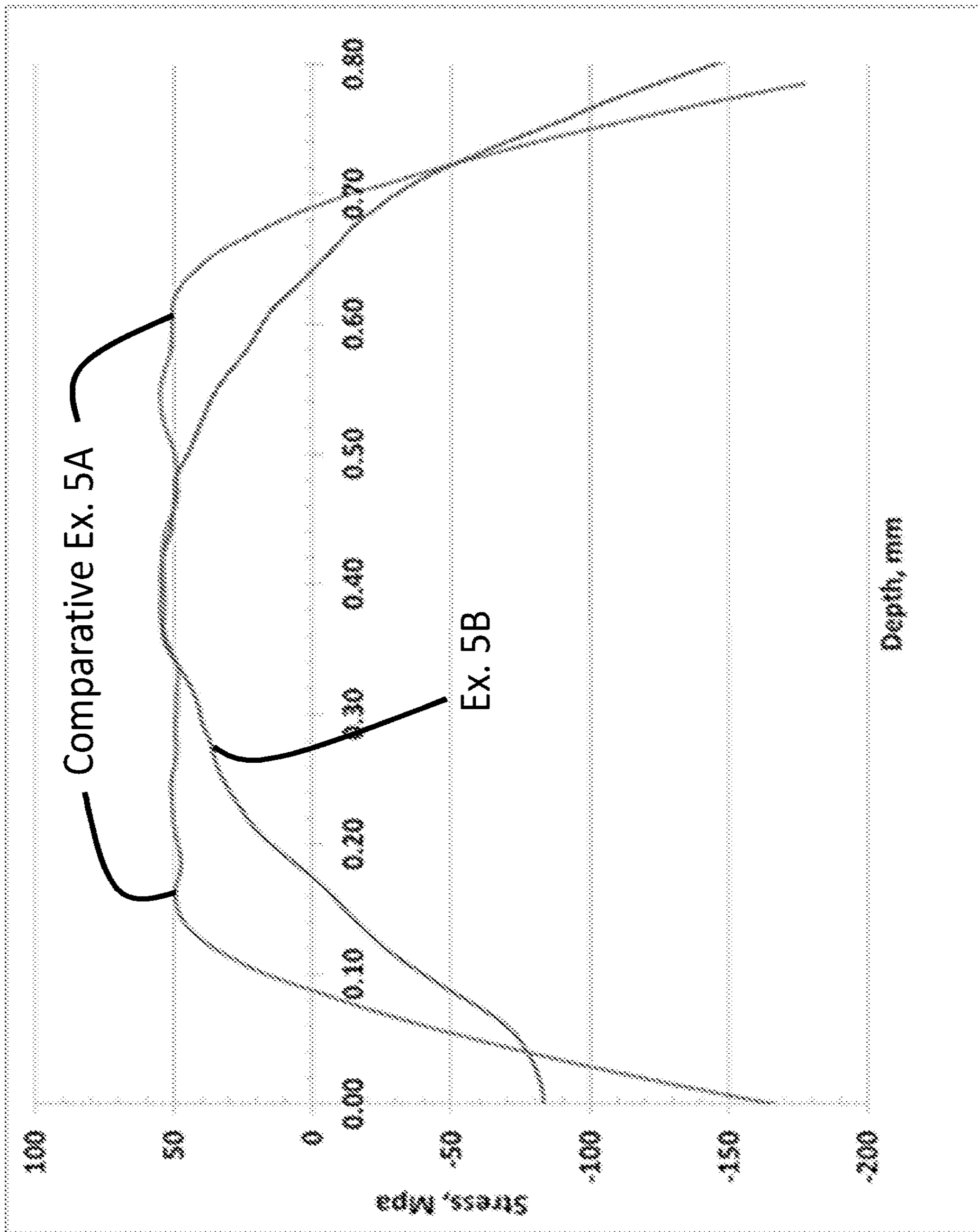

Comparative Ex. 5A
Ex. 5B
Stress, Mpa
Depth, mm
100
50
0
-50
-100
-150
-200
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80

FIG. 21

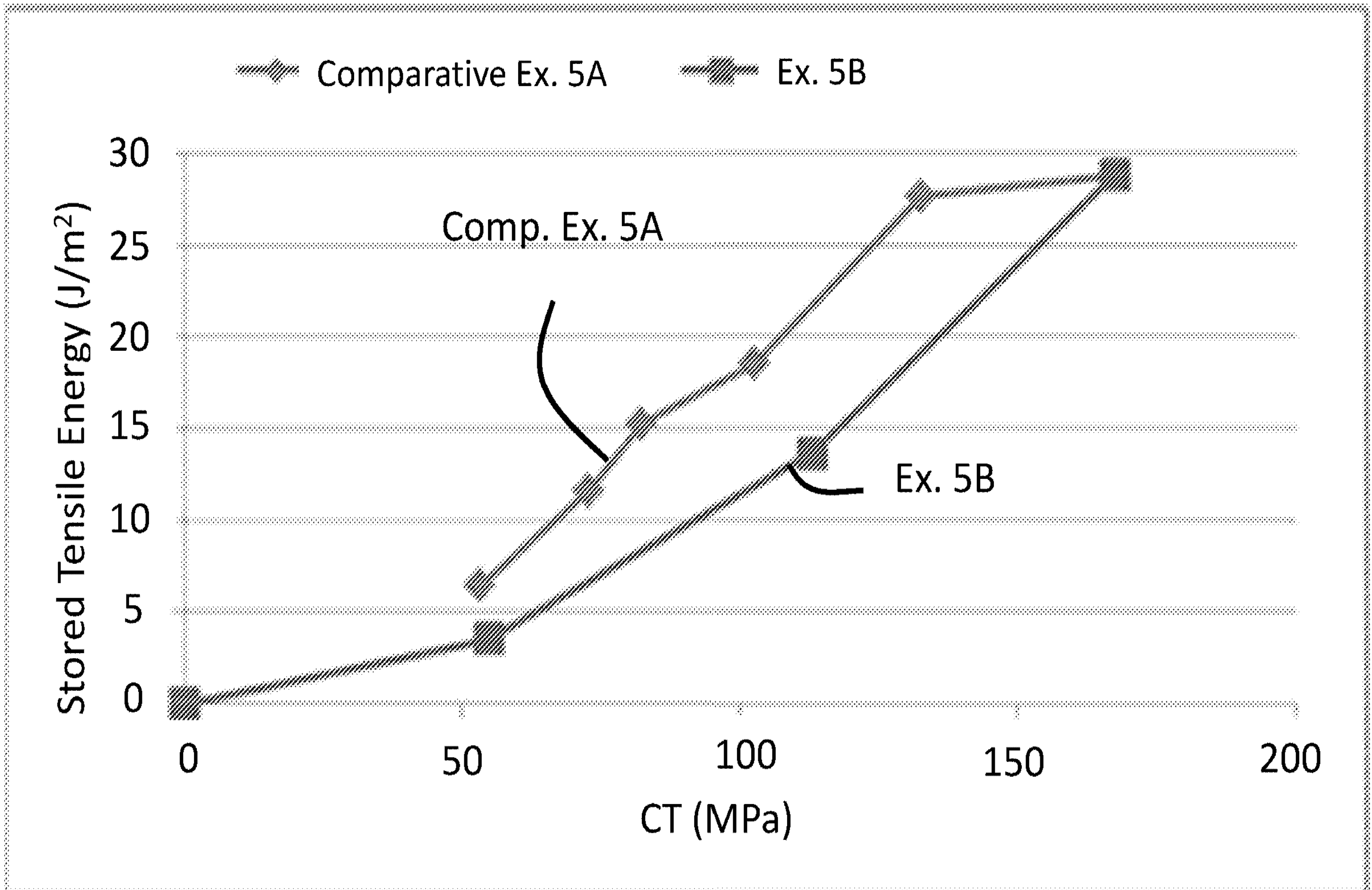
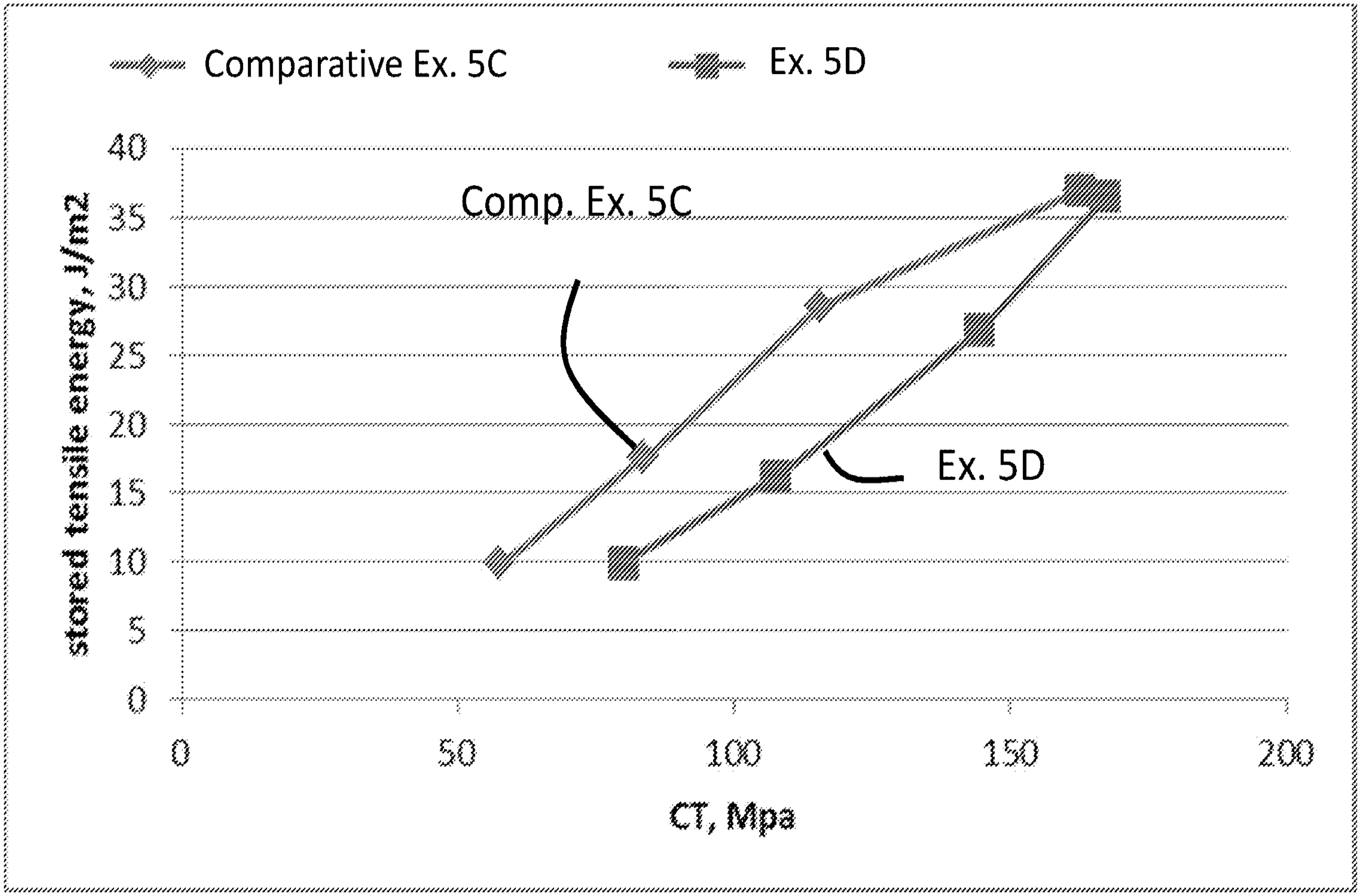

Comparative Ex. 5A
Ex. 5B
Comp. Ex. 5A
Ex. 5B
Stored Tensile Energy (J/m²)
30
25
20
15
10
5
0
0
50
100
150
200
CT (MPa)

FIG. 22


Comparative Ex. 5C
Ex. 5D
stored tensile energy, J/m2
40
35
30
25
20
15
10
5
0
0
50
100
150
200
CT, Mpa
Comp. Ex. 5C
Ex. 5D

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	FUSION-FORMABLE, GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT
First Named Inventor/Applicant Name:	Timothy Michael Gross
Filer:	Payal A. Patel/Shana Wilson
Attorney Docket Number:	SP15-410PZ

Filed as Large Entity

Filing Fees for **Provisional**

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Provisional Application Filing	1005	1	260	260
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**260**

Electronic Acknowledgement Receipt

EFS ID:	24341092
Application Number:	62266411
International Application Number:	
Confirmation Number:	7699
Title of Invention:	FUSION-FORMABLE, GLASS-BASED ARTICLES INCLUDING A METAL OXIDE CONCENTRATION GRADIENT
First Named Inventor/Applicant Name:	Timothy Michael Gross
Customer Number:	22928
Filer:	Payal A. Patel/Shana Wilson
Filer Authorized By:	Payal A. Patel
Attorney Docket Number:	SP15-410PZ
Receipt Date:	11-DEC-2015
Filing Date:	
Time Stamp:	17:14:35
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Deposit Account
Payment was successfully received in RAM	$260
RAM confirmation Number	4133
Deposit Account	033325
Authorized User	WILSON, SHANA

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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	20151207_SP15-410PZ_US_Provisional_Transmittal.pdf	318307 df85ce960bdb02e60bef849c9beb85eccd70c597	no	2
Warnings:					
Information:					
2		20151210_SP15-410PZ_US_Application.pdf	419702 a6596c5115ddbc409c0f9474b5f13fe46f0a87dc	yes	68

Multipart Description/PDF files in .zip description

Document Description	Start	End
Specification	1	55
Claims	56	67
Abstract	68	68

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
Warnings:					
Information:					
3	Drawings-only black and white line drawings	20151207_SP15-410PZ_US_Figures.pdf	617627 e397f2cc0735f73819c981bacb73d81e2694e8ff	no	22
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	30048 ba36299e5d95712d7777078afabf670c0af2e317	no	2
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New International Application Filed with the USPTO as a Receiving Office

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